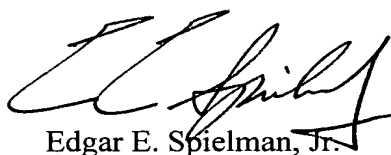


obligation to assign. Thus, the co-pending application does not constitute prior art against the present application.

For all of the foregoing reasons, reconsideration of the outstanding rejections is respectfully requested. Applicants submit that the pending claims should be deemed patentable, and thus appropriate for interference, for the same reasons as led to the allowance and issuance of the '229 patent. Declaration of an interference between the subject application and U.S. 6,156,229 is urged.

Respectfully submitted,



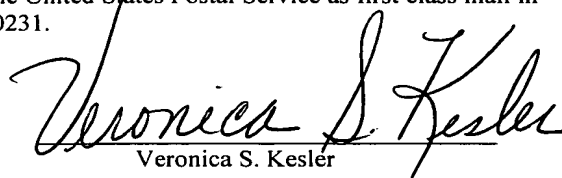
Edgar E. Spielman, Jr.  
Reg. No. 25,929  
Attorney for Applicant(s)

Telephone: (225) 388-7604

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2/20/02  
Date



Veronica S. Kesler



252	156	Subcl.
Class	ISSUE CLASSIFICA	

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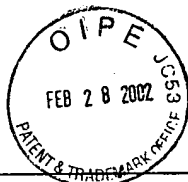
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## U.S. UTILITY PATENT APPLICATION

O.I.P.E. <i>DATE</i> SCANNED <i>DATE</i> Q.A. <i>DATE</i>	PATENT DATE DEC 05 2008
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SECTOR	CLASS	SUBCLASS	ART UNIT	EXAMINER
	20	200	100	100

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**PREPARED AND APPROVED FOR ISSUE**

ISSUING CLASSIFICATION												
ORIGINAL					CROSS REFERENCE(S)							
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<input type="checkbox"/> <b>TERMINAL DISCLAIMER</b>	<b>DRAWINGS</b>			<b>CLAIMS ALLOWED</b>	
	Sheets Drwg. _____	Figs. Drwg. _____	Print Fig. _____	Total Claims 20	Print Claim for O.G. 1
I a) The term of this patent subsequent to _____ (date) has been disclaimed.	Betsey J. Morrison (Assistant Examiner) (Date)			NOTICE OF ALLOWANCE MAILED 2-18-00	
I b) The term of this patent shall not extend beyond the expiration date of U.S. Patent No. _____	M.L. _____ 3/7/00 (Primary Examiner) (Date)			ISSUE FEE Amount Due 1216.00 Date Paid	
<input type="checkbox"/> c) The terminal _____ months of this patent have been disclaimed.	J.P. _____ 3/9/00 (Legal Instruments Examiner) (Date)			ISSUE BATCH NUMBER T 48	
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(LABEL AREA)

(FACE)

# PATENT APPLICATION



09106602

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## CONTENTS

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1. Application _____ papers.		42. _____	
2. <u>IDS</u>	<u>6-29-98</u>	43. _____	
3. <u>9/13/98 Rejection (3m)</u>	<u>9/14/99</u>	44. _____	
4. <u>Response (2/13/99)</u>	<u>12/16/99 (17m)</u>	45. _____	
5. <u>Amendment</u>	<u>2/18/00</u>	46. _____	
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POSITION	INITIALS	ID NO.	DATE
FEE DETERMINATION	<i>mp</i>		7/7/98
O.I.P.E. CLASSIFIER		10	7/7/98
FORMALITY REVIEW	<i>h.h.</i>	71629	7-12-98

INDEX OF CLAIMS

✓ ..... Rejected  
 = ..... Allowed  
 - (Through numeral) Canceled  
 + ..... Restricted  
 N ..... Non-elected  
 I ..... Interference  
 A ..... Appeal  
 O ..... Objected

Claim	Final	Original	Date
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Class	Sub.	Date	Exmr.
210	754	↓	↓
	758		
	764		
252	186.1		
423	462	↓	↓
	466	9/8/99	Bgm
Search to	date	2/15/00	Bgm
252	186.44	2/15/00	Bgm

# SEARCH NOTES

(INCLUDING SEARCH STRATEGY)

	Date	Exmr.

INTERFERENCE SEARCHED

INTERFERENCE SEARCHED			
Class	Sub.	Date	Exmr.
252	186.1 186.44		

(RIGHT OUTSIDE)



US006156229A

**United States Patent** [19]

Yang et al.

[11] **Patent Number:** 6,156,229[45] **Date of Patent:** Dec. 5, 2000

[54] **STABLE OXIDIZING BROMINE FORMULATIONS, METHOD OF MANUFACTURE AND USES THEREOF FOR BIOFOULING CONTROL**

[75] **Inventors:** Shunong Yang; William F. McCoy, both of Naperville; Anthony W. Dallmier, Aurora, all of Ill.

[73] **Assignee:** Nalco Chemical Company, Naperville, Ill.

[21] **Appl. No.:** 09/106,602

[22] **Filed:** Jun. 29, 1998

[51] **Int. Cl.<sup>7</sup>** ..... C01B 7/09

[52] **U.S. Cl.** ..... 252/186.1; 252/186.44

[58] **Field of Search** ..... 210/754, 758, 210/764; 252/186.1, 186.44; 423/462, 466

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*Primary Examiner*—David A. Simmons  
*Assistant Examiner*—Betsey J. Morrison  
*Attorney, Agent, or Firm*—Kelly L. Cummings; Thomas M. Breininger

[57] **ABSTRACT**

Stable biocide formulations containing oxidizing bromine are provided for biofouling control in industrial water systems. The formulations contain at least one stable oxidizing bromine compound that is prepared from at least one oxidizing chemical reagent, at least one bromine source and at least one bromine or halogen stabilizer. The resulting products are a mixture of stable oxidizing bromine compounds that can be used as a biocide in an industrial water system.

20 Claims, No Drawings

# STABLE OXIDIZING BROMINE FORMULATIONS, METHOD OF MANUFACTURE AND USES THEREOF FOR BIOFOULING CONTROL

## FIELD OF THE INVENTION

The present invention relates to formulations used in biofouling control in industrial water systems. More specifically, the present invention relates to methods of preparing stable oxidizing bromine formulations and their use in biofouling control in industrial water systems.

## BACKGROUND OF THE INVENTION

While elemental liquid bromine is an effective biocide, its low solubility (<4 g/100 g water), low boiling point (54.3° C.), high vapor pressure (214 mm Hg at 25° C.) and extreme corrosivity limit its use as a biocide in industrial applications. Another oxidizing bromine compound, bromate, has very little antimicrobial activity. Bromate is also very toxic to mammals and is a suspected carcinogen. Nonoxidizing inorganic bromine compounds, such as bromide, have little or no antimicrobial activity.

A mixture of an aqueous bromine solution and a bromine stabilizer has been used to generate stable oxidizing bromine compounds for use as a biocide. An unstabilized aqueous bromine solution is very acidic, unstable and emits very pungent bromine fumes. The concentration of stabilized hypobromite solution that can be made from liquid bromine, however, has been limited due to the low solubility of bromine in water.

It has also been suggested that, in addition to a bromine stabilizer, an oxidizer, such as hypochlorite, be added to activate the bromide to hypobromite. After the completion of the conversion of bromide to hypobromite, the hypobromite is stabilized by the addition of a halogen stabilizer, such as sulfamate. While this is an improved process with a higher level of oxidizing halogen content (around 14% as Br<sub>2</sub>), this process still requires the separate step of synthesizing sodium hypobromite (NaOBr) as a bromine source. NaOBr is known to be very unstable and will rapidly disproportionate to bromide and bromate, both of which have little or no antimicrobial activity. In addition, because sodium hypochlorite (NaOCl) is used as an activation agent, the concentration of stabilized product is limited by the available concentration of NaOCl.

Also known are methods of generating bromine for on-site use. Such processes involve electrolytically converting bromate into active bromine compounds such as bromine, hypobromous acid, hypobromite ion and hydrogen tribromide under acidic conditions. However, because the above process generates bromine for on-site use, methods or measures for optimizing bromine stabilization are not addressed.

Therefore, methods of generating higher concentrations of stable oxidizing bromine formulations in a safer manner are needed.

## SUMMARY OF THE INVENTION

The present invention satisfies the aforementioned needs by providing a method of generating a stable oxidizing bromine compound which includes the steps of mixing an alkali or alkaline earth metal bromide and an alkali or alkaline earth metal bromate in water to provide an aqueous solution, cooling the solution to a temperature of less than 25° C., preferably less than 20° C. and more preferably less

than 10° C., and thereafter adding a halogen stabilizer to the solution, the halogen stabilizer being selected from the group consisting of R—NH<sub>2</sub>, R—NH—R', R—SO<sub>2</sub>—NH<sub>2</sub>, R—SO<sub>2</sub>—NHR', R—CO—NH<sub>2</sub>, R—CO—NH—R' and R—CO—NH—CO—R' wherein R is a hydroxy group, an alkyl group or an aromatic group and R' is an alkyl group or an aromatic group. Preferred halogen stabilizers include urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, mono or diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine. Sulfamic acid is the most preferred halogen stabilizer.

In an embodiment, the halogen stabilizer is added to the solution in a molar amount approximately equal to the combined molar amount of alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate.

In an embodiment, the step of adding the halogen stabilizer results in the solution having a pH of less than 2.

In an embodiment, the method comprises agitating the solution for a time period of greater than 5 minutes after the step of adding the halogen stabilizer.

In an embodiment, the method comprises adjusting the solution to a pH of greater than 13 through the addition of alkali or alkaline earth metal hydroxide after the step of adding the halogen stabilizer.

In an embodiment, the step of mixing the alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate further comprises mixing the alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate in a molar ratio of alkali or alkaline earth metal bromide:bromate of about 2:1.

In an embodiment, the method of the present invention provides a stable oxidizing bromine compound which includes the steps of mixing about 2 moles of alkali or alkaline earth metal bromide and about 1 mole of alkali or alkaline earth metal bromate in water to provide an aqueous solution, followed by the step of cooling the solution to a temperature of less than 10° C., followed by the step of adding an acidic halogen stabilizer to the solution to lower the pH of the solution to less than 2, the acidic halogen stabilizer being selected from the group consisting of R—NH<sub>2</sub>, R—NH—R', R—SO<sub>2</sub>—NH<sub>2</sub>, R—SO<sub>2</sub>—NHR', R—CO—NH<sub>2</sub>, R—CO—NH—R' and R—CO—NH—CO—R' wherein R is a hydroxy group, an alkyl group or an aromatic group and R' is an alkyl group or an aromatic group. Preferred halogen stabilizers include urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, mono or diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine. The acidic halogen stabilizer is added to the solution in a molar amount approximately equal to a combined molar amount of alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate, followed by the step of agitating the solution for a time period of greater than 5 minutes, followed by the step of adding an alkali or alkaline earth metal hydroxide to the solution to increase the pH of the solution to a level greater than 13.

In an embodiment, the method of the present invention provides a method of preparing a stable oxidizing bromine compound which includes the steps of preparing a caustic solution comprising a halogen stabilizer, water and an alkali or alkaline earth metal hydroxide, adding bromine to the solution while agitating the solution and cooling the solution.

In an embodiment, the halogen stabilizer is selected from the group consisting of R—NH<sub>2</sub>, R—NH—R', R—SO<sub>2</sub>—NH<sub>2</sub>, R—SO<sub>2</sub>—NHR', R—CO—NH<sub>2</sub>, R—CO—NH—R'

and  $R-CO-NH-CO-R^1$  wherein R is a hydroxy group, an alkyl group or an aromatic group and  $R^1$  is an alkyl group or an aromatic group. Preferred halogen stabilizers include urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, mono or di ethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

In an embodiment, the caustic solution has a pH greater than 13 after the addition of bromine.

In an embodiment, the step of adding bromine is further characterized as adding bromine in a molar amount approximately equal to the molar amount of halogen stabilizer and approximately equal to one-half of the molar amount of alkali or alkaline earth metal hydroxide.

In an embodiment, the solution is cooled to a temperature of less than 25° C.

In an embodiment, the step of adding bromine is performed without exposing the bromine to air.

In an embodiment, an alkali or alkaline earth metal hydroxide is added to the solution after the addition of bromine to increase the pH of the solution above 13.

In an embodiment, the method of the present invention provides a method of preparing a stable oxidizing bromine compound in an aqueous solution which includes the steps of dissolving an alkali or alkaline earth metal bromate salt in water to form a solution, followed by the step of adding a halogen stabilizer to the solution, the halogen stabilizer being selected from the group consisting of  $R-NH_2$ ,  $R-NH-R^1$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NHR^1$ ,  $R-CO-NH_2$ ,  $R-CO-NH-R^1$  and  $R-CO-NH-CO-R^1$  wherein R is a hydroxy group, an alkyl group or an aromatic group and  $R^1$  is an alkyl group or an aromatic group. Preferred halogen stabilizers include urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, mono or di ethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine. Following the addition of the halogen stabilizer, bromine is added to the solution.

In an embodiment, a step of cooling the solution to a temperature of less than 25° C., preferably less than 15° C. and more preferably less than 10° C., is performed simultaneously with the step of adding the bromine to the solution.

In an embodiment, the present invention provides an aqueous biocide solution containing a stable oxidizing bromine formulation. The solution comprises at least one oxidizing bromine compound selected from the group consisting of  $SO_3NHBr$  and  $SO_3NBr_2$  when sulfamate is used as the bromine stabilizer and a base in an amount sufficient to raise the pH of the solution to a level greater than 13.

In an embodiment, the base in the solution is an alkali or alkaline earth metal hydroxide.

It is therefore an advantage of the present invention to generate a stable oxidizing bromine solution using liquid bromine in a safe and efficient manner whereby no bromine fumes are generated.

It is another advantage of the present invention to generate a higher concentration of stabilized hypobromite without the need for a separate step for hypobromite generation.

Another advantage of the present invention is that it provides a method for generating water soluble solid stable oxidizing bromine compounds.

Still another advantage of the present invention is that it provides a method for generating stable oxidizing bromine compounds without unwanted by-products such as high levels of bromate.

Still another advantage of the present invention is that the method of the present invention does not generate chloride

and therefore the method of the present invention provides stable oxidizing bromine formulations that are less corrosive.

Yet another advantage of the present invention is that it provides stable oxidizing bromine compounds that are safer to transport and that are non-acidic.

Yet another advantage of the present invention is that it generates stable oxidizing bromine compounds for biofouling control in industrial water systems that are more compatible with other water treatment chemicals than unstabilized oxidizing bromine compounds.

The industrial water systems include cooling water systems, cooling ponds, reservoirs, sweetwater applications, decorative fountains, pasteurizers, evaporative condensers, hydrostatic sterilizers and retorts, gas scrubber systems and air washer systems.

Another advantage of the present invention is that it provides an improved method of biofouling control in pulp and paper processing systems.

Another advantage of the present invention is that it provides an improved method of biofouling control occurring on the surfaces of equipment in contact with produced oil field waters.

Another advantage of the present invention is that it provides an improved method of biofouling control in a food processing system.

Yet another advantage of the present invention is that it provides improved biofouling control in a beverage processing system.

Still another advantage of the present invention is that it provides improved biofouling control in a recreational water system.

Another advantage of the present invention is that it provides an improved method of disinfecting a hard surface.

Another advantage of the present invention is that it provides an improved bleaching method for the laundering of soiled garments and for the manufacture of cellulosic materials.

And, another advantage of the present invention is that it provides an improved method of washing food items, such as fruit and other food items.

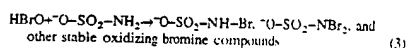
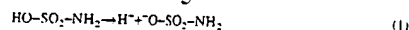
Other objects and advantages of the present invention will be apparent upon a review of the following detailed description and appended claims.

#### DETAILED DESCRIPTION OF THE INVENTION

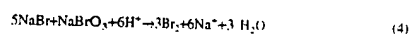
The present invention provides a plurality of formulations and methods for generating a wide concentration of stable oxidizing bromine compounds for biofouling control in cooling water and other industrial systems.

In an embodiment, the strategy employed by the present invention utilizes a mixture of alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate in water as the bromine source. Bromate also serves as an oxidizing agent. The molar ratio of bromide to bromate is optimally 2:1. The solution is then cooled to a temperature preferably of less than 25° C. and even more preferably of less than 10° C. An acidic stabilizer or acidic stabilizing solution, such as sulfamic acid, is then added to the solution to lower the pH of the solution to less than 2. Additional stabilizer is then added to achieve equal molar amounts relative to bromine for optimal stabilization. Without being limited by theory, the following reactions are believed to occur:





Since bromide, bromate and sulfamate co-exist in the resulting solution, reaction (1) to reaction (3) occurs sequentially with respect to each other. Without being limited by theory, the existence of an oxidizing bromine stabilizer and correct bromide to bromate ratio are believed to prevent the formation of bromine according to the following reaction:



If reaction (4) were to happen instead of reaction (2), half of the raw bromine source would convert back to non-biocidal and non-oxidizing bromide according to reaction (5):



However, an analysis of products prepared in accordance with the present invention confirms that the reaction yield is higher than 50%. In fact, more than 80% of the bromine source was converted to oxidized bromine forms. Accordingly, the reaction yield of at least 80% was achieved.

The reaction time for reactions 1-3 at a pH of less than 2 ranges from 5 to 10 minutes with good agitation. If the product is not going to be used immediately, a strong base, such as NaOH, is added to raise the product pH to a level greater than 13 making the product thermally stable. During the pH adjustment, temperature control is important because the temperature increase by the heat generated from the acid-base reaction can cause the product to decompose. Accordingly, cooling may be necessary.

The product made with the above process has good thermostability and a high total available halogen concentration, as high as 34% as  $\text{Br}_2$ .

#### EXAMPLES

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

##### Example I

By way of an example, synthesis of a stable oxidizing bromine product in accordance with the above-described method is carried out by mixing 21.2 grams of  $\text{NaBrO}_3$ , 32.8 grams of NaBr and 100 grams of water, cooling the solution to 3° C., adding 48 grams of sulfamic acid to the solution and agitating the solution for 10 minutes. Then, 48 grams of 50% aqueous NaOH is added slowly to the solution while controlling the solution temperature to a range between 4° C. and 14° C. The resulting product was a golden yellow solution with a pH of 13.77 and available halogen concentration of 25.1% as  $\text{Br}_2$ . In this example, the theoretical  $\text{Br}_2\%$  is 29.9 if all of the bromine sources (bromide and bromate) were to convert to stable oxidizing bromines. Therefore, the yield is about 84%.

##### Example II

By way of another example, synthesis of stable oxidizing bromine formulations in accordance with the above-described method is carried out by mixing 21.2 grams of  $\text{NaBrO}_3$ , 32.8 grams of NaBr and 100 grams of water in a

reactor, cooling the solution to 3° C., adding 44 grams of sulfamic acid to the solution and agitating the solution for 10 minutes, slowly adding 43 grams of 50% aqueous NaOH while controlling the reactor temperature between 3° C. and 14° C. The resulting product was a golden yellow solution with a pH of 14.11 and available halogen concentration of 27.7% as  $\text{Br}_2$ . In this example, the theoretical  $\text{Br}_2\%$  is 31.2 if all of the bromine sources (bromide and bromate) are converted into stable oxidizing bromines. Therefore, the product yield is about 88.8%.

In another embodiment, liquid bromine is used as both oxidizer and bromine source. Sulfamate or other nitrogen base compounds are used as stabilizers. In addition, an adequate amount of alkali or alkaline earth metal hydroxide is required to maintain product pH. Formulation temperature is also extremely critical in insuring the formation of stable oxidizing bromines. Without adequate pH and temperature control, the heat generated by the exothermic reaction will cause rapid decomposition of the oxidizing species.

The process of making high concentration stable oxidizing bromine formulations consists of two steps. In the first step, a caustic stabilizing solution is prepared by mixing sulfamic acid, water and alkali or alkaline metal hydroxides (preferably NaOH,  $\text{Mg}(\text{OH})_2$  or other hydroxides). The pH of the alkali or alkaline earth metal sulfamate solution is higher than 14. Excess hydroxides are purposely added to neutralize the acids generated by the subsequent bromination step and to maintain a high pH (preferably greater than 13) in the finished product. The preferred molar ratio of sulfamate to liquid bromine is 1:1. The preferred molar ratio of hydroxide to liquid bromine is 2.2:1. The stabilizer solution can also be obtained by dissolving alkali or alkaline metal sulfamate in water and adding an appropriate amount of hydroxide.

The process is normally carried out in a jacketed glass reactor equipped with a proper mixing device. A cooling system for the reactor should be set up so that the reactor temperature can be controlled at an optimal range. An excessively high reaction temperature during the bromination step will accelerate sulfamate hydrolysis and cause decomposition of the desired product.

The second step of the process is to slowly add liquid bromine into the stabilizer solution under good agitation. Bromine is preferably added directly into the stabilizer solution through a Teflon® tube to prevent elemental bromine exposure to air. The addition rate is controlled so that the reaction temperature is preferably below 25° C. The higher the reaction temperature, the lower the product yield. If the reaction temperature gets over 35° C., sulfamate will start hydrolyzing into sulfate and ammonium. The resulting ammonium will react with and consume hypobromite and produce nitrogen gas which can be observed as vigorous foaming. With proper addition rates of liquid bromine, the liquid bromine will react instantaneously and will be stabilized. The process does not produce detectable bromine fumes.

The product made with the above-described process was found to include no detectable bromate (less than 50 ppm with ion chromatography analysis); no detectable product concentration change was observed during a 2 month storage period at room temperature. For a 16.2% (as  $\text{Br}_2$ ) product, the product has a half life of 74.5 days at 57° C.

##### Example III

By way of an example, synthesis of a stable oxidizing bromine product using the above-described method is

achieved by mixing 52.16 grams of sulfamic acid, 42.0 grams of water and 128.0 grams of 50% aqueous NaOH in a 500 ml three-neck glass reactor. The mixture is cooled to a temperature of about 3° C. under constant agitation and refrigerated in a water bath. 82.5 grams of liquid bromine (99.8% Br<sub>2</sub>) is slowly added to the solution and the reaction temperature is controlled and maintained below 10° C. The resulting solution has a pH of 12.5. The solution pH was increased to a level greater than 13 by adding 3.0 grams of 50% NaOH. The bromine content in the resulting solution was 26.2% as Br<sub>2</sub> while a theoretical content if 100% conversion is achieved is 27.0% as Br<sub>2</sub>.

After overnight storage at room temperature (21° C.), the formation of large amounts of crystals was observed in the solution. Using a 0.45 µm filter to separate the crystal from the liquid, followed by dehydration of the crystals under vacuum overnight, 46.8% as Br<sub>2</sub> was detected in the solid product while 18.7% of bromine content as Br<sub>2</sub> remained in the liquid. The solid product was found to be extremely water soluble. Accordingly, the present invention provides a solid stable oxidizing bromine product which is water soluble.

The solid product obtained in the above example has a very high concentration of stable oxidizing bromine compounds. The remaining content is believed to be water, excess NaOH and NaBr.

Other hybrid methods can be used to generate stable oxidizing bromine compounds. One such method consists of using bromate salt as an oxidizer and bromine source, liquid bromine as an oxidizer, bromine source and acidic compound and sulfamate or another suitable halogen stabilizer as the bromine stabilizer. The reaction mechanism would be as follows:



The process can be carried out by dissolving bromate salt and water, adding sulfamate or other stabilizer to the solution; slowly adding liquid bromine, adjusting the pH to a level greater than 13 by adding NaOH, if the resulting product is to be stored for a long period of time. The process should be conducted at a temperature less than 25° C., especially during the addition of liquid bromine.

In an embodiment, the stable oxidizing bromine compound of the present invention can be used to provide improved biofouling control in industrial water systems, pulp and paper processing systems, food and beverage processing systems and recreational water systems. The stable oxidizing bromine compound of the present invention can also be used as a bleaching agent and to disinfect a hard surface. By way of example only, the present invention may be added to an aqueous media used to transport food through various processing systems and also to disinfect process equipment and waste water streams.

It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the present invention and without diminishing its attendant advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

What is claimed is:

1. A method of generating a stable oxidizing bromine compound, the method comprising the following steps:

mixing an alkali or alkaline earth metal bromide and an alkali or alkaline earth metal bromate in water to provide an aqueous solution, cooling the solution to a temperature less than 25° C., and adding a halogen stabilizer to the solution, the halogen stabilizer being selected from the group consisting of R—NH<sub>2</sub>, R—NH—R', R—SO<sub>2</sub>—NH<sub>2</sub>, R—SO<sub>2</sub>—NHR', R—CO—NH<sub>2</sub>, R—CO—NH—R' and R—CO—NH—CO—R' wherein R is a hydroxy group, an alkyl group or an aromatic group and R' is an alkyl group or an aromatic group.

2. The method of claim 1 wherein the halogen stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

3. The method of claim 1 wherein the halogen stabilizer is added in a molar amount approximately equal to a combined molar amount of alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate.

4. The method of claim 1 wherein the halogen stabilizer is sulfamic acid.

5. The method of claim 1 wherein the step of adding the halogen stabilizer results in the solution having a pH of less than 2.

6. The method of claim 1 further comprising the following step after the step of adding the halogen stabilizer: agitating the solution for a time period greater than 5 minutes.

7. The method of claim 1 further comprising the following step after the step of adding the halogen stabilizer: adjusting the solution to a pH of greater than 13.

8. The method of claim 1 wherein the step of mixing the alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate further comprising mixing the alkali or alkaline earth metal bromide and the alkali or alkaline earth metal bromate in a molar ratio of alkali or alkaline earth metal bromide:bromate of about 2:1.

9. A method of generating a stable oxidizing bromine compound, the method comprising the following steps:

mixing about 2 moles of alkali or alkaline earth metal bromide and about 1 mole of alkali or alkaline earth metal bromate in water to provide an aqueous solution, cooling the solution to a temperature of less than 10° C., adding an acidic halogen stabilizer to the solution to lower the pH of the solution to less than 2, the acidic halogen stabilizer being selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine, the acidic halogen stabilizer being added in a molar amount approximately equal to a combined molar amount of alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate,

agitating the solution for a time period greater than 5 minutes, and

adding an alkali or alkaline earth metal hydroxide to the solution to increase the pH of the solution to greater than 13.

10. A method of generating a stable oxidizing bromine compound, the method comprising the following steps: preparing a caustic solution comprising a halogen stabilizer, water and an alkali or alkaline earth metal

hydroxide, the halogen stabilizer being selected from the group consisting of  $R-NH_2$ ,  $R-NH-R^1$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NHR^1$ ,  $R-CO-NH_2$ ,  $R-CO-NH-R^1$  and  $R-CO-NH-CO-R^1$  wherein R is a hydroxy group, an alkyl group or an aromatic group and R<sup>1</sup> is an alkyl group or an aromatic group.

adding bromine to the solution while mixing the solution, and

cooling the solution.

11. The method of claim 10 wherein the halogen stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

12. The method of claim 10 wherein the caustic solution has a pH after the addition of bromine of greater than 13.

13. The method of claim 10 wherein the step of adding bromine is further characterized as adding bromine in a molar amount approximately equal to a molar amount of halogen stabilizer and approximately one-half of a molar amount of alkali or alkaline earth metal hydroxide.

14. The method of claim 10 wherein the cooling step is further characterized as cooling the solution to a temperature of less than 25° C.

15. The method of claim 10 wherein the step of adding bromine is performed without exposing the bromine to air.

16. The method of claim 10 further comprising the following step after the addition of the bromine:

adding an alkali or alkaline earth metal hydroxide to the solution to increase the pH of the solution above 13.

17. A method of generating a stable oxidizing bromine compound, the method comprising the following steps:

preparing a caustic solution comprising a halogen stabilizer, water and an alkali or alkaline earth metal hydroxide, the halogen stabilizer being selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine,

diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

adding bromine to the solution in a molar amount approximately equal to a molar amount of halogen stabilizer and approximately one-half of a molar amount of alkali or alkaline earth metal hydroxide and without exposing the bromine to air.

mixing the solution, the solution having a pH after the mixing step of greater than 13.

cooling the solution to a temperature of less than 25° C., and

adding an alkali or alkaline earth metal hydroxide to the solution to increase the pH of the solution above 13.

18. A method of generating a stable oxidizing bromine compound in an aqueous solution, the method comprising the following steps:

dissolving an alkali or alkaline earth metal bromate salt in water to form a solution,

adding a halogen stabilizer to the solution, the halogen stabilizer being selected from the group consisting of  $R-NH_2$ ,  $R-NH-R^1$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NHR^1$ ,  $R-CO-NH_2$ ,  $R-CO-NH-R^1$  and  $R-CO-NH-CO-R^1$  wherein R is a hydroxy group, an alkyl group or an aromatic group and R<sup>1</sup> is an alkyl group or an aromatic group, and

adding bromine to the solution.

19. The method of claim 18 wherein the halogen stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

20. The method of claim 18 further comprising the following step performed simultaneously with the step of adding bromine:

cooling the solution to a temperature of less than 25° C.

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PATENT APPLICATION SERIAL NO. \_\_\_\_\_

U.S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICE  
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APPLICANT	<p>SHUNONG YANG, NAPERVILLE, IL; WILLIAM F. MCCOY, NAPERVILLE, IL; ANTHONY W. DALLMIER, AURORA, IL.</p> <p><b>**CONTINUING DOMESTIC DATA*****</b> VERIFIED <u>Bgm</u></p> <p><b>**371 (NAT'L STAGE) DATA*****</b> VERIFIED <u>Bgm</u></p> <p><b>**FOREIGN APPLICATIONS*****</b> VERIFIED <u>Bgm</u></p> <p>FOREIGN FILING LICENSE GRANTED 07/16/98</p>
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Foreign Priority claimed 35 USC 119 (a-d) conditions met <input type="checkbox"/> yes <input checked="" type="checkbox"/> no Verified and Acknowledged <u>Bgm</u> <small>Examiner's Initials</small>	STATE OR COUNTRY IL	SHEETS DRAWING 0	TOTAL CLAIMS 57	INDEPENDENT CLAIMS 10
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TITLE	STABLE OXIDIZING BROMINE FORMULATIONS, METHOD OF MANUFACTURE AND USES THEREOF FOR BIOFOULING CONTROL
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JC604 U.S. PTO  
06/29/98

# UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

ASSISTANT COMMISSIONER FOR PATENTS

Box Patent Application  
WASHINGTON, D.C. 20231

Docket No.: 5458

Sir:

Transmitted herewith for filing is the patent application of:

Inventor: Shunong Yang, et al.

For: STABLE OXIDIZING BROMINE FORMULATIONS, METHOD OF MANUFACTURE AND USES THEREOF FOR BIOFOULING CONTROL

Enclosed are:

- ☒ Specification Total Pages 34
- ☐ Drawings Total Sheets 0
- ☒ Oath or Declaration Total Pages 2
  - 1. ☒ Newly executed (original or copy)
  - 2. ☐ Copy from a prior application (37 CFR 1.63(d))(for divisional)

☐ DELETION OF INVENTOR(S)

Signed statement attached deleting inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).

- ☐ Incorporation By Reference (useable if Box 2 is checked) The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 2, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.
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  - ☐ Cancel in this application original claims          of the prior application before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)

Claims as Filed				
For	Number Filed	Number Extra	Rate	Basic Fee \$790.00
Total Claims	57-20 =	37 =	X \$22 =	814.00
Independent Claims	10-3 =	7 =	X \$82 =	574.00
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Total Filing Fee →				2178.00
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The Commissioner is hereby authorized to charge any additional fees which may be required for, or during, the pendency of this application, or credit any overpayment to Deposit Account No. 14-0105.

Respectfully submitted,

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Elizabeth A. Troscinski  
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No. 5458

STABLE OXIDIZING BROMINE FORMULATIONS,  
METHOD OF MANUFACTURE AND USES  
THEREOF FOR BIOFOULING CONTROL

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### ABSTRACT

Stable biocide formulations containing oxidizing bromine are provided for biofouling control in industrial water systems. The formulations contain at least one stable oxidizing bromine compound that is prepared from at least one oxidizing chemical reagent, at least one bromine source and at least one bromine or halogen stabilizer. The resulting products are a mixture of stable oxidizing bromine compounds that can be used as a biocide in an industrial water system.

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### FIELD OF THE INVENTION

The present invention relates to formulations used in biofouling control in industrial water systems. More specifically, the present invention relates to methods of preparing stable oxidizing bromine formulations and their use in biofouling control in industrial water systems.

### BACKGROUND OF THE INVENTION

While elemental liquid bromine is an effective biocide, its low solubility (< 4g/100g water), low boiling point (54.3°C), high vapor pressure (214 mm Hg at 25°C) and extreme corrosivity limit its use as a biocide in industrial applications. Another oxidizing bromine compound, bromate, has very little antimicrobial activity. Bromate is also very toxic to mammals and is a suspected carcinogen. Nonoxidizing inorganic bromine compounds, such as bromide, have little or no antimicrobial activity.

A mixture of an aqueous bromine solution and a bromine stabilizer has been used to generate stable oxidizing bromine compounds for use as a biocide. An unstabilized aqueous bromine solution is very acidic, unstable and emits very pungent bromine fumes. The concentration of stabilized hypobromite solution that can be made from liquid bromine, however, has been limited due to the low solubility of bromine in water.

It has also been suggested that, in addition to a bromine stabilizer, an oxidizer, such as hypochlorite, be added to activate the bromide to hypobromite. After the completion of the conversion of bromide to hypobromite, the hypobromite is stabilized by the addition of a halogen stabilizer, such as sulfamate. While this is an improved process with a higher level of oxidizing halogen content (around 14% as Br<sub>2</sub>), this process

still requires the separate step of synthesizing sodium hypobromite (NaOBr) as a bromine source. NaOBr is known to be very unstable and will rapidly disproportionate to bromide and bromate, both of which have little or no antimicrobial activity. In addition, because sodium hypochlorite (NaOCl) is used as an activation agent, the concentration of  
5 stabilized product is limited by the available concentration of NaOCl.

Also known are methods of generating bromine for on-site use. Such processes involve electrolytically converting bromate into active bromine compounds such as bromine, hypobromous acid, hypobromite ion and hydrogen tribromide under acidic conditions. However, because the above process generates bromine for on-site use,  
10 methods or measures for optimizing bromine stabilization are not addressed.

Therefore, methods of generating higher concentrations of stable oxidizing bromine formulations in a safer manner are needed.

#### SUMMARY OF THE INVENTION

The present invention satisfies the aforementioned needs by providing a method  
15 of generating a stable oxidizing bromine compound which includes the steps of mixing an alkali or alkaline earth metal bromide and an alkali or alkaline earth metal bromate in water to provide an aqueous solution, cooling the solution to a temperature of less than 25°C, preferably less than 20°C and more preferably less than 10°C, and thereafter adding a halogen stabilizer to the solution, the halogen stabilizer being selected from the  
20 group consisting of R-NH<sub>2</sub>, R-NH-R<sup>1</sup>, R-SO<sub>2</sub>-NH<sub>2</sub>, R-SO<sub>2</sub>-NHR<sup>1</sup>, R-CO-NH<sub>2</sub>, R-CO-NH-R<sup>1</sup> and R-CO-NH-CO-R<sup>1</sup> wherein R is a hydroxy group, an alkyl group or an aromatic group and R<sup>1</sup> is an alkyl group or an aromatic group. Preferred halogen stabilizers

include urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, mono or diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine. Sulfamic acid is the most preferred halogen stabilizer.

In an embodiment, the halogen stabilizer is added to the solution in a molar  
5 amount approximately equal to the combined molar amount of alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate.

In an embodiment, the step of adding the halogen stabilizer results in the solution having a pH of less than 2.

In an embodiment, the method comprises agitating the solution for a time period  
10 of greater than 5 minutes after the step of adding the halogen stabilizer.

In an embodiment, the method comprises adjusting the solution to a pH of greater than 13 through the addition of alkali or alkaline earth metal hydroxide after the step of adding the halogen stabilizer.

In an embodiment, the step of mixing the alkali or alkaline earth metal bromide  
15 and alkali or alkaline earth metal bromate further comprises mixing the alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate in a molar ratio of alkali or alkaline earth metal bromide:bromate of about 2:1.

In an embodiment, the method of the present invention provides a stable oxidizing bromine compound which includes the steps of mixing about 2 moles of alkali or alkaline  
20 earth metal bromide and about 1 mole of alkali or alkaline earth metal bromate in water to provide an aqueous solution, followed by the step of cooling the solution to a temperature of less than 10°C, followed by the step of adding an acidic halogen stabilizer to the

solution to lower the pH of the solution to less than 2, the acidic halogen stabilizer being selected from the group consisting of  $R-NH_2$ ,  $R-NH-R^1$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NHR^1$ ,  $R-CO-NH_2$ ,  $R-CO-NH-R^1$  and  $R-CO-NH-CO-R^1$  wherein R is a hydroxy group, an alkyl group or an aromatic group and  $R^1$  is an alkyl group or an aromatic group. Preferred  
5 halogen stabilizers include urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, mono or di ethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine. The acidic halogen stabilizer is added to the solution in a molar amount approximately equal to a combined molar amount of alkali or alkaline earth metal  
10 bromide and alkali or alkaline earth metal bromate, followed by the step of agitating the solution for a time period of greater than 5 minutes, followed by the step of adding an alkali or alkaline earth metal hydroxide to the solution to increase the pH of the solution to a level greater than 13.

In an embodiment, the method of the present invention provides a method of preparing a stable oxidizing bromine compound which includes the steps of preparing a  
15 caustic solution comprising a halogen stabilizer, water and an alkali or alkaline earth metal hydroxide, adding bromine to the solution while agitating the solution and cooling the solution.

In an embodiment, the halogen stabilizer is selected from the group consisting of  $R-NH_2$ ,  $R-NH-R^1$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NHR^1$ ,  $R-CO-NH_2$ ,  $R-CO-NH-R^1$  and  $R-CO-NH-$   
20  $CO-R^1$  wherein R is a hydroxy group, an alkyl group or an aromatic group and  $R^1$  is an alkyl group or an aromatic group. Preferred halogen stabilizers include urea, thiourea,

creatinine, cyanuric acids, alkyl hydantoins, mono or di ethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

In an embodiment, the caustic solution has a pH greater than 13 after the addition of bromine.

5 In an embodiment, the step of adding bromine is further characterized as adding bromine in a molar amount approximately equal to the molar amount of halogen stabilizer and approximately equal to one-half of the molar amount of alkali or alkaline earth metal hydroxide.

In an embodiment, the solution is cooled to a temperature of less than 25°C.

10 In an embodiment, the step of adding bromine is performed without exposing the bromine to air.

In an embodiment, an alkali or alkaline earth metal hydroxide is added to the solution after the addition of bromine to increase the pH of the solution above 13.

In an embodiment, the method of the present invention provides a method of  
15 preparing a stable oxidizing bromine compound in an aqueous solution which includes the steps of dissolving an alkali or alkaline earth metal bromate salt in water to form a solution, followed by the step of adding a halogen stabilizer to the solution, the halogen stabilizer being selected from the group consisting of  $R-NH_2$ ,  $R-NH-R^1$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NHR^1$ ,  $R-CO-NH_2$ ,  $R-CO-NH-R^1$  and  $R-CO-NH-CO-R^1$  wherein R is a hydroxy  
20 group, an alkyl group or an aromatic group and  $R^1$  is an alkyl group or an aromatic group. Preferred halogen stabilizers include urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, mono or di ethanolamine, organic sulfonamides, biuret, sulfamic acid,

organic sulfamates and melamine. Following the addition of the halogen stabilizer, bromine is added to the solution.

In an embodiment, a step of cooling the solution to a temperature of less than 25°C, preferably less than 15°C and more preferably less than 10°C, is performed  
5 simultaneously with the step of adding the bromine to the solution.

In an embodiment, the present invention provides an aqueous biocide solution containing a stable oxidizing bromine formulation. The solution comprises at least one oxidizing bromine compound selected from the group consisting of  $\text{SO}_3\text{NHBr}$  and  $\text{SO}_3\text{NBr}_2$  when sulfamate is used as the bromine stabilizer and a base in an amount  
10 sufficient to raise the pH of the solution to a level greater than 13.

In an embodiment, the base in the solution is an alkali or alkaline earth metal hydroxide.

It is therefore an advantage of the present invention to generate a stable oxidizing bromine solution using liquid bromine in a safe and efficient manner whereby no bromine  
15 fumes are generated.

It is another advantage of the present invention to generate a higher concentration of stabilized hypobromite without the need for a separate step for hypobromite generation.

Another advantage of the present invention is that it provides a method for  
20 generating water soluble solid stable oxidizing bromine compounds.

Still another advantage of the present invention is that it provides a method for generating stable oxidizing bromine compounds without unwanted by-products such as high levels of bromate.

5 Still another advantage of the present invention is that the method of the present invention does not generate chloride and therefore the method of the present invention provides stable oxidizing bromine formulations that are less corrosive.

Yet another advantage of the present invention is that it provides stable oxidizing bromine compounds that are safer to transport and that are non-acidic.

10 Yet another advantage of the present invention is that it generates stable oxidizing bromine compounds for biofouling control in industrial water systems that are more compatible with other water treatment chemicals than unstabilized oxidizing bromine compounds.

15 The industrial water systems include cooling water systems, cooling ponds, reservoirs, sweetwater applications, decorative fountains, pasteurizers, evaporative condensers, hydrostatic sterilizers and retorts, gas scrubber systems and air washer systems.

Another advantage of the present invention is that it provides an improved method of biofouling control in pulp and paper processing systems.

20 Another advantage of the present invention is that it provides an improved method of biofouling control occurring on the surfaces of equipment in contact with produced oil field waters.

Another advantage of the present invention is that it provides an improved method of biofouling control in a food processing system.

Yet another advantage of the present invention is that it provides improved biofouling control in a beverage processing system.

5 Still another advantage of the present invention is that it provides improved biofouling control in a recreational water system.

Another advantage of the present invention is that it provides an improved method of disinfecting a hard surface.

10 Another advantage of the present invention is that it provides an improved bleaching method for the laundering of soiled garments and for the manufacture of cellulosic materials.

And, another advantage of the present invention is that it provides an improved method of washing food items, such as fruit and other food items.

15 Other objects and advantages of the present invention will be apparent upon a review of the following detailed description and appended claims.

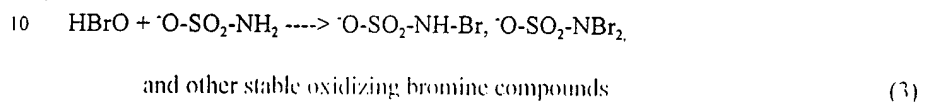
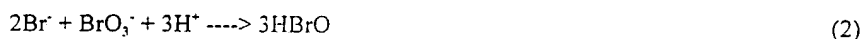
#### DETAILED DESCRIPTION OF THE INVENTION

20 The present invention provides a plurality of formulations and methods for generating a wide concentration of stable oxidizing bromine compounds for biofouling control in cooling water and other industrial systems.

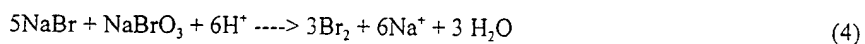
In an embodiment, the strategy employed by the present invention utilizes a mixture of alkali or alkaline earth metal bromide and alkali or alkaline earth metal



bromate in water as the bromine source. Bromate also serves as an oxidizing agent. The molar ratio of bromide to bromate is optimally 2:1. The solution is then cooled to a temperature preferably of less than 25°C and even more preferably of less than 10°C. An acidic stabilizer or acidic stabilizing solution, such as sulfamic acid, is then added to the solution to lower the pH of the solution to less than 2. Additional stabilizer is then added to achieve equal molar amounts relative to bromine for optimal stabilization. Without being limited by theory, the following reactions are believed to occur:



Since bromide, bromate and sulfamate co-exist in the resulting solution, reaction (1) to reaction (3) occurs sequentially with respect to each other. Without being limited by theory, the existence of an oxidizing bromine stabilizer and correct bromide to bromate ratio are believed to prevent the formation of bromine according to the following reaction:



If reaction (4) were to happen instead of reaction (2), half of the raw bromine source would convert back to non-biocidal and non-oxidizing bromide according to reaction (5):



However, an analysis of products prepared in accordance with the present invention confirms that the reaction yield is higher than 50%. In fact, more than 80% of the bromine source was converted to oxidized bromine forms. Accordingly, the reaction yield of at least 80% was achieved.

5        The reaction time for reactions 1-3 at a pH of less than 2 ranges from 5 to 10 minutes with good agitation. If the product is not going to be used immediately, a strong base, such as NaOH, is added to raise the product pH to a level greater than 13 making the product thermally stable. During the pH adjustment, temperature control is important because the temperature increase by the heat generated from the acid-base reaction can  
10        cause the product to decompose. Accordingly, cooling may be necessary.

The product made with the above process has good thermostability and a high total available halogen concentration, as high as 34% as Br<sub>2</sub>.

#### EXAMPLES

The following examples are intended to be illustrative of the present invention  
15        and to teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

#### Example I

By way of an example, synthesis of a stable oxidizing bromine product in accordance with the above-described method is carried out by mixing 21.2 grams of  
20        NaBrO<sub>3</sub>, 32.8 grams of NaBr and 100 grams of water, cooling the solution to 3°C, adding 48 grams of sulfamic acid to the solution and agitating the solution for 10 minutes. Then, 48 grams of 50% aqueous NaOH is added slowly to the solution while controlling the

solution temperature to a range between 4°C and 14°C. The resulting product was a golden yellow solution with a pH of 13.77 and available halogen concentration of 25.1% as Br<sub>2</sub>. In this example, the theoretical Br<sub>2</sub>% is 29.9 if all of the bromine sources (bromide and bromate) were to convert to stable oxidizing bromines. Therefore, the yield is about 84%.

#### Example II

By way of another example, synthesis of stable oxidizing bromine formulations in accordance with the above-described method is carried out by mixing 21.2 grams of NaBrO<sub>3</sub>, 32.8 grams of NaBr and 100 grams of water in a reactor, cooling the solution to 3°C, adding 44 grams of sulfamic acid to the solution and agitating the solution for 10 minutes, slowly adding 43 grams of 50% aqueous NaOH while controlling the reactor temperature between 3°C and 14°C. The resulting product was a golden yellow solution with a pH of 14.11 and available halogen concentration of 27.7% as Br<sub>2</sub>. In this example, the theoretical Br<sub>2</sub>% is 31.2 if all of the bromine sources (bromide and bromate) are converted into stable oxidizing bromines. Therefore, the product yield is about 88.8%.

In another embodiment, liquid bromine is used as both oxidizer and bromine source. Sulfamate or other nitrogen base compounds are used as stabilizers. In addition, an adequate amount of alkali or alkaline earth metal hydroxide is required to maintain product pH. Formulation temperature is also extremely critical in insuring the formation of stable oxidizing bromines. Without adequate pH and temperature control, the heat generated by the exothermic reaction will cause rapid decomposition of the oxidizing species.

The process of making high concentration stable oxidizing bromine formulations consists of two steps. In the first step, a caustic stabilizing solution is prepared by mixing sulfamic acid, water and alkali or alkaline metal hydroxides (preferably NaOH,  $Mg(OH)_2$  or other hydroxides). The pH of the alkali or alkaline earth metal sulfamate solution is  
5 higher than 14. Excess hydroxides are purposely added to neutralize the acids generated by the subsequent bromination step and to maintain a high pH (preferably greater than 13) in the finished product. The preferred molar ratio of sulfamate to liquid bromine is 1:1. The preferred molar ratio of hydroxide to liquid bromine is 2.2:1. The stabilizer solution can also be obtained by dissolving alkali or alkaline metal sulfamate in water and  
10 adding an appropriate amount of hydroxide.

The process is normally carried out in a jacketed glass reactor equipped with a proper mixing device. A cooling system for the reactor should be set up so that the reactor temperature can be controlled at an optimal range. An excessively high reaction temperature during the bromination step will accelerate sulfamate hydrolysis and cause  
15 decomposition of the desired product.

The second step of the process is to slowly add liquid bromine into the stabilizer solution under good agitation. Bromine is preferably added directly into the stabilizer solution through a Teflon<sup>®</sup> tube to prevent elemental bromine exposure to air. The addition rate is controlled so that the reaction temperature is preferably below 25°C. The  
20 higher the reaction temperature, the lower the product yield. If the reaction temperature gets over 35°C, sulfamate will start hydrolyzing into sulfate and ammonium. The resulting ammonium will react with and consume hypobromite and produce nitrogen gas

which can be observed as vigorous foaming. With proper addition rates of liquid bromine, the liquid bromine will react instantaneously and will be stabilized. The process does not produce detectable bromine fumes.

The product made with the above-described process was found to include no  
5 detectable bromate (less than 50 ppm with ion chromatography analysis); no detectable product concentration change was observed during a 2 month storage period at room temperature. For a 16.2% (as Br<sub>2</sub>) product, the product has a half life of 74.5 days at 57°C.

### Example III

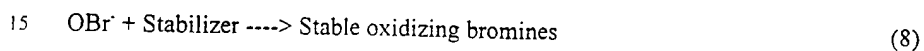
10 By way of an example, synthesis of a stable oxidizing bromine product using the above-described method is achieved by mixing 52.16 grams of sulfamic acid, 42.0 grams of water and 128.0 grams of 50% aqueous NaOH in a 500 ml three-neck glass reactor. The mixture is cooled to a temperature of about 3°C under constant agitation and refrigerated in a water bath. 82.5 grams of liquid bromine (99.8% Br<sub>2</sub>) is slowly added to  
15 the solution and the reaction temperature is controlled and maintained below 10°C. The resulting solution has a pH of 12.5. The solution pH was increased to a level greater than 13 by adding 3.0 grams of 50% NaOH. The bromine content in the resulting solution was 26.2% as Br<sub>2</sub> while a theoretical content if 100% conversion is achieved is 27.0% as Br<sub>2</sub>.

20 After overnight storage at room temperature (21°C), the formation of large amounts of crystals was observed in the solution. Using a 0.45 µm filter to separate the crystal from the liquid, followed by dehydration of the crystals under vacuum overnight,

46.8% as Br<sub>2</sub> was detected in the solid product while 18.7% of bromine content as Br<sub>2</sub> remained in the liquid. The solid product was found to be extremely water soluble. Accordingly, the present invention provides a solid stable oxidizing bromine product which is water soluble.

5       The solid product obtained in the above example has a very high concentration of stable oxidizing bromine compounds. The remaining content is believed to be water, excess NaOH and NaBr.

Other hybrid methods can be used to generate stable oxidizing bromine compounds. One such method consists of using bromate salt as an oxidizer and bromine  
10       source, liquid bromine as an oxidizer, bromine source and acidic compound and sulfamate or another suitable halogen stabilizer as the bromine stabilizer. The reaction mechanism would be as follows:



The process can be carried out by dissolving bromate salt and water, adding sulfamate or other stabilizer to the solution, slowly adding liquid bromine, adjusting the pH to a level greater than 13 by adding NaOH, if the resulting product is to be stored for a long period of time. The process should be conducted at a temperature less than 25°C,  
20       especially during the addition of liquid bromine.

In an embodiment, the stable oxidizing bromine compound of the present invention can be used to provide improved biofouling control in industrial water systems,

pulp and paper processing systems, food and beverage processing systems and recreational water systems. The stable oxidizing bromine compound of the present invention can also be used as a bleaching agent and to disinfect a hard surface. By way of example only, the present invention may be added to an aqueous media used to transport  
5 food through various processing systems and also to disinfect process equipment and waste water streams.

It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the  
10 present invention and without diminishing its attendant advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

WHAT IS CLAIMED IS:

1. A method of generating a stable oxidizing bromine compound, the method comprising the following steps:

mixing an alkali or alkaline earth metal bromide and an alkali or alkaline earth

5 metal bromate in water to provide an aqueous solution,

cooling the solution to a temperature less than 25°C, and

adding a halogen stabilizer to the solution, the halogen stabilizer being selected from the group consisting of R-NH<sub>2</sub>, R-NH-R<sup>1</sup>, R-SO<sub>2</sub>-NH<sub>2</sub>, R-SO<sub>2</sub>-NHR<sup>1</sup>, R-CO-NH<sub>2</sub>, R-CO-NH-R<sup>1</sup> and R-CO-NH-CO-R<sup>1</sup> wherein R is a hydroxy group, an alkyl group or an aromatic group and R<sup>1</sup> is an alkyl group or an aromatic group.

2. The method of claim 1 wherein the halogen stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

3. The method of claim 1 wherein the halogen stabilizer is added in a molar amount approximately equal to a combined molar amount of alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate.

4. The method of claim 1 wherein the halogen stabilizer is sulfamic acid.



5. The method of claim 1 wherein the step of adding the halogen stabilizer results in the solution having a pH of less than 2.

5 6. The method of claim 1 further comprising the following step after the step of adding the halogen stabilizer:

agitating the solution for a time period greater than 5 minutes.

7. The method of claim 1 further comprising the following step after the step of  
10 adding the halogen stabilizer:

adjusting the solution to a pH of greater than 13.

8. The method of claim 1 wherein the step of mixing the alkali or alkaline earth  
metal bromide and alkali or alkaline earth metal bromate further comprising mixing the  
15 alkali or alkaline earth metal bromide and the alkali or alkaline earth metal bromate in a  
molar ratio of alkali or alkaline earth metal bromide:bromate of about 2:1.

9. A stable oxidizing bromine compound prepared by the following steps:  
mixing an alkali or alkaline earth metal bromide and an alkali or alkaline earth metal bromate in water to provide an aqueous solution,  
cooling the solution to a temperature less than 25°C, and  
5 adding a halogen stabilizer to the solution, the halogen stabilizer being selected from the group consisting of R-NH<sub>2</sub>, R-NH-R<sup>1</sup>, R-SO<sub>2</sub>-NH<sub>2</sub>, R-SO<sub>2</sub>-NHR<sup>1</sup>, R-CO-NH<sub>2</sub>, R-CO-NH-R<sup>1</sup> and R-CO-NH-CO-R<sup>1</sup> wherein R is a hydroxy group, an alkyl group or an aromatic group and R<sup>1</sup> is an alkyl group or an aromatic group.
- 10 10. The stable oxidizing bromine compound of claim 9 wherein the halogen stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoin, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.
- 15 11. In a method for the control of biofouling in an industrial water system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 9.
12. In a method for the control of biofouling in a pulp and paper processing system in  
20 which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 9.

13. In a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field waters in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 9.

14. In a method for the control of biofouling in a food processing system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 9.

15. In a method for the control of biofouling in a beverage processing system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 9.

16. In a method for the control of biofouling in a recreational water system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 9.

17. In a method of disinfecting a hard surface in which an oxidizing agent is added to disinfect the hard surface, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 9.

18. In a method of washing food items in which an oxidizing agent is added to disinfect the food items, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 9.

19. In a method of laundering soiled garments and manufacturing cellulosic materials in which an oxidizing agent is used as a bleaching agent, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 9.

20. <sup>9</sup> A method of generating a stable oxidizing bromine compound, the method comprising the following steps:

mixing about 2 moles of alkali or alkaline earth metal bromide and about 1 mole of alkali or alkaline earth metal bromate in water to provide an aqueous solution,

5 cooling the solution to a temperature of less than 10°C,

adding an acidic halogen stabilizer to the solution to lower the pH of the solution to less than 2, the acidic halogen stabilizer being selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine,

10 diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine, the acidic halogen stabilizer being added in a molar amount approximately equal to a combined molar amount of alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate,

agitating the solution for a time period greater than 5 minutes, and

15 adding an alkali or alkaline earth metal hydroxide to the solution to increase the pH of the solution to greater than 13.

21. A stable oxidizing bromine compound prepared by the following steps:  
mixing about 2 moles of alkali or alkaline earth metal bromide and about 1 mole  
of alkali or alkaline earth metal bromate in water to provide an aqueous solution,  
cooling the solution to a temperature of less than 10°C,  
5 adding an acidic halogen stabilizer to the solution to lower the pH of the solution  
to less than 2, the acidic halogen stabilizer being selected from the group consisting of  
urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine,  
diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and  
melamine, the acidic halogen stabilizer being added in a molar amount approximately  
10 equal to a combined molar amount of alkali or alkaline earth metal bromide and alkali or  
alkaline earth metal bromate,  
agitating the solution for a time period greater than 5 minutes, and  
adding an alkali or alkaline earth metal hydroxide to the solution to increase the  
pH of the solution to greater than 13.

15 22. In a method for the control of biofouling in an industrial water system in which an  
oxidizing agent is added to control the biofouling, the method comprising using as the  
oxidizing agent the stable oxidizing bromine compound of claim 21.

10 23. A method of generating a stable oxidizing bromine compound, the method comprising the following steps:

preparing a caustic solution comprising a halogen stabilizer, water and an alkali or alkaline earth metal hydroxide, the halogen stabilizer being selected from the group  
5 consisting of  $R-NH_2$ ,  $R-NH-R'$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NHR'$ ,  $R-CO-NH_2$ ,  $R-CO-NH-R'$  and  $R-CO-NH-CO-R'$  wherein  $R$  is a hydroxy group, an alkyl group or an aromatic group and  $R'$  is an alkyl group or an aromatic group,

adding bromine to the solution while mixing the solution, and  
cooling the solution.

10 24. The method of claim 23 wherein the halogen stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

15 25. The method of claim 23 wherein the caustic solution has a pH after the addition of bromine of greater than 13.

20 26. The method of claim 23 wherein the step of adding bromine is further characterized as adding bromine in a molar amount approximately equal to a molar amount of halogen stabilizer and approximately one-half of a molar amount of alkali or alkaline earth metal hydroxide.

27. The method of claim 23 wherein the cooling step is further characterized as cooling the solution to a temperature of less than 25°C.
28. The method of claim 23 wherein the step of adding bromine is performed without exposing the bromine to air.
29. The method of claim 23 further comprising the following step after the addition of the bromine:
- adding an alkali or alkaline earth metal hydroxide to the solution to increase the pH of the solution above 13.
30. A stable oxidizing bromine compound prepared by the following steps:
- preparing a caustic solution comprising a halogen stabilizer, water and an alkali or alkaline earth metal hydroxide, the halogen stabilizer being selected from the group consisting of  $R-NH_2$ ,  $R-NH-R^1$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NH-R^1$ ,  $R-CO-NH_2$ ,  $R-CO-NH-R^1$  and  $R-CO-NH-CO-R^1$  wherein R is a hydroxy group, an alkyl group or an aromatic group and  $R^1$  is an alkyl group or an aromatic group,
- adding bromine to the solution while mixing the solution, and
- cooling the solution.



31. The stable oxidizing bromine compound of claim 30 wherein the halogen stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

32. In a method for the control of biofouling in an industrial water system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 30.

33. In a method for the control of biofouling in a pulp and paper processing system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 30.

34. In a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field waters in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 30.

35. In a method for the control of biofouling in a food processing system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 30.

36. In a method for the control of biofouling in a beverage processing system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 30.

5 37. In a method for the control of biofouling in a recreational water system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 30.

38. In a method of disinfecting a hard surface in which an oxidizing agent is added to  
10 disinfect the hard surface, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 30.

39. In a method of washing food items in which an oxidizing agent is added to  
disinfect the food items, the method comprising using as the oxidizing agent the stable  
15 oxidizing bromine compound of claim 30.

40. In a method of laundering soiled garments and manufacturing cellulosic materials in which an oxidizing agent is used as a bleaching agent, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 30.

41 A method of generating a stable oxidizing bromine compound, the method comprising the following steps:

preparing a caustic solution comprising a halogen stabilizer, water and an alkali or alkaline earth metal hydroxide, the halogen stabilizer being selected from the group  
5 consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine,

adding bromine to the solution in a molar amount approximately equal to a molar amount of halogen stabilizer and approximately one-half of a molar amount of alkali or  
10 alkaline earth metal hydroxide and without exposing the bromine to air,

mixing the solution, the solution having a pH after the mixing step of greater than  
13,

cooling the solution to a temperature of less than 25°C, and

adding an alkali or alkaline earth metal hydroxide to the solution to increase the  
15 pH of the solution above 13.

42. A stable oxidizing bromine compound prepared by the following steps:

preparing a caustic solution comprising a halogen stabilizer, water and an alkali or alkaline earth metal hydroxide, the halogen stabilizer being selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins,

5 monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine,

adding bromine to the solution in a molar amount approximately equal to a molar amount of halogen stabilizer and approximately one-half of a molar amount of alkali or alkaline earth metal hydroxide and without exposing the bromine to air,

10 mixing the solution, the solution having a pH after the mixing step of greater than 13,

cooling the solution to a temperature of less than 25°C, and

adding an alkali or alkaline earth metal hydroxide to the solution to increase the pH of the solution above 13.

15

43. In a method for the control of biofouling in an industrial water system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 42.

44.18 A method of generating a stable oxidizing bromine compound in an aqueous solution, the method comprising the following steps:

dissolving an alkali or alkaline earth metal bromate salt in water to form a solution,

5 adding a halogen stabilizer to the solution, the halogen stabilizer being selected from the group consisting of  $R-NH_2$ ,  $R-NH-R^1$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NHR^1$ ,  $R-CO-NH_2$ ,  $R-CO-NH-R^1$  and  $R-CO-NH-CO-R^1$  wherein R is a hydroxy group, an alkyl group or an aromatic group and  $R^1$  is an alkyl group or an aromatic group, and adding bromine to the solution.

10 45.19 The method of claim 44 wherein the halogen stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

15 20 46.18 The method of claim 44 further comprising the following step performed simultaneously with the step of adding bromine:  
cooling the solution to a temperature of less than 25°C.

47. A stable oxidizing bromine compound prepared by the following steps:  
dissolving an alkali or alkaline earth metal bromate salt in water to form a  
solution,

adding a halogen stabilizer to the solution, the halogen stabilizer being selected  
5 from the group consisting of  $R-NH_2$ ,  $R-NH-R^1$ ,  $R-SO_2-NH_2$ ,  $R-SO_2-NHR^1$ ,  $R-CO-NH_2$ ,  $R-$   
 $CO-NH-R^1$  and  $R-CO-NH-CO-R^1$  wherein R is a hydroxy group, an alkyl group or an  
aromatic group and  $R^1$  is an alkyl group or an aromatic group, and  
adding bromine to the solution.

10 48. The stable oxidizing bromine compound of claim 47 wherein the halogen  
stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric  
acids, alkyl hydantoin, monoethanolamine, diethanolamine, organic sulfonamides,  
biuret, sulfamic acid, organic sulfamates and melamine.

15 49. In a method for the control of biofouling in an industrial water system in which an  
oxidizing agent is added to control the biofouling, the method comprising using as the  
oxidizing agent the stable oxidizing bromine compound of claim 47.

20 50. In a method for the control of biofouling in a pulp and paper processing system in  
which an oxidizing agent is added to control the biofouling, the method comprising using  
as the oxidizing agent the stable oxidizing bromine compound of claim 47.

51. In a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field waters in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 47.

5

52. In a method for the control of biofouling in a food processing system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 47.

10 53. In a method for the control of biofouling in a beverage processing system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 47.

15 54. In a method for the control of biofouling in a recreational water system in which an oxidizing agent is added to control the biofouling, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 47.

20 55. In a method of disinfecting a hard surface in which an oxidizing agent is added to disinfect the hard surface, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 47.

56. In a method of washing food items in which an oxidizing agent is added to disinfect the food items, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 47.

5 57. In a method of laundering soiled garments and manufacturing cellulosic materials in which an oxidizing agent is used as a bleaching agent, the method comprising using as the oxidizing agent the stable oxidizing bromine compound of claim 47.



## DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that: Shunong Yang/William F. McCoy/Anthony W. Dallmier

My residence, post office address, and citizenship are as stated below next to my name, I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which the patent is sought on the invention entitled: STABLE OXIDIZING BROMINE FORMULATIONS, METHOD OF MANUFACTURE AND USES THEREOF FOR BIOFOULING CONTROL

the specification of which

(check one)      ( X )      is attached hereto  
                          ( )      was filed on \_\_\_\_\_ as

Application Serial N° \_\_\_\_\_  
 and was amended on \_\_\_\_\_

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by an amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119, of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

### Prior Foreign Applications

### Priority Claimed

_____ (Number)	_____ (Country)	_____ (Day/Mo./Yr. filed)	( ) Yes ( ) No
_____ (Number)	_____ (Country)	_____ (Day/Mo./Yr. filed)	( ) Yes ( ) No
_____ (Number)	_____ (Country)	_____ (Day/Mo./Yr. filed)	( ) Yes ( ) No

I hereby claim the benefit under Title 35, United States Code, §120, of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

_____ (Application Serial N°)	_____ (Filing Date)	_____ (Status - Patented, pending, abandoned)
_____ (Application Serial N°)	_____ (Filing Date)	_____ (Status - Patented, pending, abandoned)

**POWER OF ATTORNEY:** I, a named inventor, I hereby appoint the following attorneys and/or agents to prosecute this application and transact all business in the Patent & Trademarks Office connected therewith.

Thomas M. Breininger, Reg. No. 29,897  
 Kelly L. Cummings, Reg. No. 39,646  
 Margaret Meta Brumm, Reg. No. 33,655

SEND CORRESPONDENCE TO:

Direct telephone calls to:

Kelly L. Cummings  
 Patent & Licensing Department  
 Nalco Chemical Company  
 One Nalco Center  
 Naperville, Illinois 60563-1198

Kelly L. Cummings  
 Patent Department  
 630-305-2328

I further declare that all statements, data, and figures made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

I also believe that disclosures, statements, data, and figures included in the above mentioned specification and claims are, to my best knowledge, accurate and truthful.

Full name of sole or first inventor Shunong YangInventor's Signature [Signature]Date 6/25/98 Country of Citizenship ChinaResidence Naperville, IllinoisPost Office Address 1708 Warbler Drive, Naperville, Illinois 60565Full name of second inventor William F. McCoyInventor's Signature [Signature]Date 6/25/98 Country of Citizenship USAResidence Naperville, IllinoisPost Office Address 735 Thornapple Drive, Naperville, Illinois 60540Full name of third inventor Anthony W. DallmierInventor's Signature [Signature]Date 6/25/98 Country of Citizenship USAResidence Aurora, IllinoisPost Office Address 1683 Kautz Road, Aurora, Illinois 60504

Full name of fourth inventor \_\_\_\_\_

Inventor's Signature \_\_\_\_\_

Date \_\_\_\_\_ Country of Citizenship \_\_\_\_\_

Residence \_\_\_\_\_

Post Office Address \_\_\_\_\_

PATENT  
In the United States Patent and Trademark Office

Applicant: Shunong Yang, et al. ) Art Unit:  
Serial No: ) Examiner:  
Date Filed: ) Attorney Docket No: 5458  
Invention: Stable Oxidizing Bromine Formulations, )  
Method of Manufacture and Uses )  
Thereof For Biofouling Control )



*112*

INFORMATION DISCLOSURE STATEMENT  
UNDER 37 C.F.R. §§ 1.97 and 1.98

Honorable Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

Dear Sir:

In compliance with the duty of disclosure under 37 C.F.R. § 1.56, it is respectfully requested that this Information Disclosure Statement be entered and the references listed on attached Form PTO-1449 be considered by the Examiner and made of record. Copies of the listed references are enclosed for the convenience of the Examiner.

In accordance with 37 C.F.R. § 1.97(b), this Information Disclosure Statement is not to be construed as a representation that a search has been made or that no other possibly material information as defined in 37 C.F.R. § 1.56(a) exists.

Signed in Naperville, County of DuPage and State of Illinois this 29<sup>th</sup> day  
of June, 1998.

Respectfully submitted,

Kelly L. Cummings  
Kelly L. Cummings, Reg. No. 39,646

Nalco Chemical Company  
Patent & Licensing Department  
One Nalco Center  
Naperville, IL 60563-1198

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Form PTO 1449 U.S. Dept. of Commerce  
LIST OF PRIOR ART CITED BY APPLICANT

Atty Docket No. 3

Serial  
09/106,602

Applicant: Shunong Yang, et al.

Filing Date:

Group: 1724

U. S. PATENTS DOCUMENTS

Exam. Init.		Document No.	Date	Name	Class	Sub-Class	Filing date
Bgm	AA	3,222,276	12/65	Belohlav, et al.			
	AB	3,493,654	2/70	Goodenough, et al.			
	AC	3,558,503	1/71	Goodenough, et al.			
	AD	4,759,852	7/88	Trulear			
	AE	4,992,209	2/91	Smyk, et al.			
	AF	5,264,136	11/93	Howarth, et al.			
	AG	5,589,106	12/96	Shim, et al.			
	AH	5,603,840	2/97	Strittmatter, et al.			
Bgm	AI	5,683,654	11/97	Dallmier, et al.			
	AJ						
	AK						

FOREIGN PATENT DOCUMENTS

Exam. Init.		Document No.	Date	Country	Class	Sub-Class	Filing date
Bgm	AL	WO96/30562	10/96	PCT			3/96
	AM	0 168 253 A2	1/86	EPO			7/85
	AN	WO97/20909	6/97	PCT			12/95
Bgm	AO	WO97/43392	11/97	PCT			5/96

OTHER PRIOR ART (Including Author, Title, Date, Pertinent Pages, Etc.)

	AP		
	AQ		
	AR		
	AS		
	AT		

Examiner

Date Considered

Betsy J. Morrison

September 8, 1999



**UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office**

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
09/106,602	06/29/98	YANG	S 5458

KELLY L CUMMINGS  
PATENT & LICENSING DEPARTMENT  
NALCO CHEMICAL COMPANY  
ONE NALCO CENTER  
NAPERVILLE IL 60563-1198

IM62/0914

EXAMINER

MORRISON, B

ART UNIT	PAPER NUMBER
----------	--------------

1724

DATE MAILED:

09/14/98

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner of Patents and Trademarks

# Office Action Summary

Application No.  
09/106,602

Applicant(s)  
Yang et al.

Examiner  
Betsey Morrison

Group Art Unit  
1724



☒ Responsive to communication(s) filed on Jun 29, 1998

☐ This action is FINAL.

☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11; 453 O.G. 213.

A shortened statutory period for response to this action is set to expire 3 month(s), or thirty days, whichever is longer, from the mailing date of this communication. Failure to respond within the period for response will cause the application to become abandoned. (35 U.S.C. § 133). Extensions of time may be obtained under the provisions of 37 CFR 1.136(a).

## Disposition of Claims

☒ Claim(s) 1-57 is/are pending in the application.

Of the above, claim(s) 9-19, 21, 22, 30-40, 42, 43, and 47-57 is/are withdrawn from consideration.

☒ Claim(s) 44-46 is/are allowed.

☒ Claim(s) 1-8, 20, 23-29, and 41 is/are rejected.

☐ Claim(s) \_\_\_\_\_ is/are objected to.

☒ Claims 1-57 are subject to restriction or election requirement.

## Application Papers

☐ See the attached Notice of Draftsperson's Patent Drawing Review, PTO-948.

☐ The drawing(s) filed on \_\_\_\_\_ is/are objected to by the Examiner.

☐ The proposed drawing correction, filed on \_\_\_\_\_ is ☐ approved ☐ disapproved.

☐ The specification is objected to by the Examiner.

☐ The oath or declaration is objected to by the Examiner.

## Priority under 35 U.S.C. § 119

☐ Acknowledgement is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d).

☐ All ☐ Some\* ☐ None of the CERTIFIED copies of the priority documents have been received.

☐ received in Application No. (Series Code/Serial Number) \_\_\_\_\_

☐ received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

\*Certified copies not received: \_\_\_\_\_

☐ Acknowledgement is made of a claim for domestic priority under 35 U.S.C. § 119(e).

## Attachment(s)

☒ Notice of References Cited, PTO-892

☒ Information Disclosure Statement(s), PTO-1449, Paper No(s). 3

☐ Interview Summary, PTO-413

☐ Notice of Draftsperson's Patent Drawing Review, PTO-948

☐ Notice of Informal Patent Application, PTO-152

--- SEE OFFICE ACTION ON THE FOLLOWING PAGES ---

Art Unit: 1724

1. Restriction to one of the following inventions is required under 35 U.S.C. 121:
  - I. Claims 1-8, 20, 23-29, 41 and 44-46, drawn to a method of generating a stable oxidizing bromine compound, classified in class 423, subclass 462.
  - II. Claims 9, 10, 21, 30, 31, 42, 47 and 48, drawn to a stable oxidizing bromine compound, classified in class 252, subclass 186.1.
  - III. Claims 11-19, 22, 32-40, 43 and 49-57, drawn to methods employing the use of a stable oxidizing bromine compound, classified in class 210, subclass 754.
2. The inventions are distinct, each from the other because of the following reasons:

Inventions II and I are related as process of making and product made. The inventions are distinct if either or both of the following can be shown: (1) that the process as claimed can be used to make other and materially different product or (2) that the product as claimed can be made by another and materially different process (MPEP § 806.05(f)). In the instant case the product as claimed can be made by a materially different process, such as a process including a step of adding a different halogen stabilizer than those recited in the instant claims.
3. Inventions I and III are related as process of making and process of using the product. A three-way restriction may be made where a process of making is distinct from the product (MPEP § 806.05(I)). In this case, the product and process of making are shown to be distinct above, and thus the restriction between the process of making the product and process of using the product is proper.

Art Unit: 1724

4. Inventions II and III are related as product and process of use. The inventions can be shown to be distinct if either or both of the following can be shown: (1) the process for using the product as claimed can be practiced with another materially different product or (2) the product as claimed can be used in a materially different process of using that product (MPEP § 806.05(h)). In the instant case the process for using the product as claimed can be practice with another materially different product, such as chlorine in the case of controlling biofouling in a recreational water system.
5. Because these inventions are distinct for the reasons given above and have acquired a separate status in the art as shown by their different classification, restriction for examination purposes as indicated is proper.
6. During a telephone conversation with Ms. Kelly Cummings on September 9, 1999 a provisional election was made without traverse to prosecute the invention of Group I, claims 1-8, 20, 23-29, 41 and 44-46. Affirmation of this election must be made by applicant in replying to this Office action. Claims 9-19, 21, 22, 30-40, 42, 43 and 47-57 are withdrawn from further consideration by the examiner, 37 CFR 1.142(b), as being drawn to a non-elected invention.
7. Applicant is reminded that upon the cancellation of claims to a non-elected invention, the inventorship must be amended in compliance with 37 CFR 1.48(b) if one or more of the currently named inventors is no longer an inventor of at least one claim remaining in the application. Any amendment of inventorship must be accompanied by a petition under 37 CFR 1.48(b) and by the fee required under 37 CFR 1.17(l).



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8. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

9. Claims 1-8 and 20 are rejected under 35 U.S.C. 103(a) as being unpatentable over Dallmier et al. (in U.S. Patent No. 5,942,126: abstract; column 1, lines 17-32; column 4, lines 1-15; column 8, line 60-column 9, line 3).

Dallmier et al. disclose a process to manufacture stabilized alkali or alkaline earth metal hypobromite comprising the steps of mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide source, which forms aqueous alkali or alkaline earth metal hypobromite, and adding to the aqueous solution a stabilizer. The stabilizer may be any of various stabilizers, but the preferred stabilizers are selected from the group consisting of urea, thiourea, creatinine, cyanuric acid, alkyl hydantoins, mono or di ethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine. It is submitted that during the first step of the process of Dallmier et al., at least some alkali or alkaline earth metal bromide and bromate will inherently form and be mixed in the water and present in the resulting aqueous solution. The final product has a pH of 8 to 14, preferable 11 to 14, which includes the pH of instant claim 7.

The claims differ from Dallmier et al. by reciting a step of cooling the aqueous solution to a specific temperature (claims 1 and 20), that the halogen stabilizer is added in a specific amount

Art Unit: 1724

(claims 3 and 20), that the addition of the stabilizer results in a solution having a specific pH (claims 5 and 20), that the solution is agitated for a specific period of time after addition of the stabilizer (claims 6 and 20), and that the bromide and bromate in the aqueous solution are mixed in a specific ratio (claims 8 and 20).

It is submitted that while Dallmier et al. do not disclose cooling the aqueous solution to a specific temperature, the process of Dallmier et al. includes a step of allowing a reaction to form alkali or alkaline earth metal hypobromite, and it would have been obvious to one of ordinary skill in the art to have allowed the solution to stand and cool to ensure that a complete reaction took place. It is also submitted that one of ordinary skill in the art would have been expected to arrive at the optimum amount of stabilizer, specific pH, time for agitation, and mixture ratios by routine experimentation. Therefore, it would have been obvious to one of ordinary skill in the art to have added the amount of stabilizer recited in instant claim 3, to have achieved the pH of instant claim 5, to have agitated for the time of instant claim 6, and to have allowed the reaction to form the hypobromite for a period of time to achieve in the solution the ratio of bromide and bromate recited in instant claim 8, in order to achieve optimum operating conditions, depending on the specific results desired, absent a sufficient showing of unexpected results.

10. Claims 23-29 and 41 are rejected under 35 U.S.C. 103(a) as being unpatentable over Goodenough et al. (column 1, line 64-column 2, line 51).

Goodenough et al. disclose stable bromo-sulfamate compositions that are produced by contacting an aqueous solution of bromine, a bromine stabilizer, and a hydroxide. The stabilizer

Art Unit: 1724

and hydroxide of Goodenough et al. include the stabilizers and hydroxides of the instant claims. Goodenough et al. do not disclose exposing bromine to air.

The claims differ from Goodenough et al. by reciting a specific order of steps, preparing a solution of stabilizer and hydroxide and then adding bromine thereto, and cooling the solution (claims 23 and 41) to a specific temperature (claims 27 and 41), obtaining a solution of a specific pH (claims 25, 29 and 41), and using specific molar ratios of components (claims 26 and 41).

[It is submitted that Goodenough et al. disclose that the order of addition of reagents to water or an aqueous solution of the other reagents is not critical to the operability of the invention. Therefore, one of ordinary skill in the art would have been expected to have arrived at the optimum order of addition of reagents by routine experimentation. It would have been obvious to one of ordinary skill in the art to have added reagents in the order recited in the instant claims in order to optimize the process of making the product, depending on the results desired, absent a sufficient showing of unexpected results.] It is also submitted that one of ordinary skill in the art would have been expected to have arrived at the optimum pH values, ratio of components, and temperature to cool the solution by routine experimentation. ] Therefore, it would have been obvious to one of ordinary skill in the art to have used the pH values, ratio of components, and temperature to cool the solution recited in the instant claims in order to optimize the process of making the product, depending on the results desired, absent a sufficient showing of unexpected results.

11. Claims 44-46 are allowed.

Art Unit: 1724

12. The following is a statement of reasons for the indication of allowable subject matter:

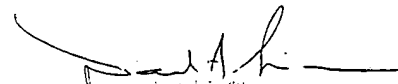
Claims 44-46 are allowed because the prior art of record fails to teach, disclose, or fairly suggest a method of generating a stable oxidizing bromine compound comprising dissolving an alkali or alkaline method bromate salt in water, adding a stabilizer to the resulting solution, and then adding bromine to the solution.


13. The prior art made of record and not relied upon is considered pertinent to Applicant's disclosure.

14. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Betsey Morrison whose telephone number is (703) 305-3934. The examiner can normally be reached on Monday through Thursday from 8:30 AM to 6:00 PM, and on alternate Fridays from 8:30 AM to 5:00 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Mr. David Simmons, can be reached at (703) 308-1972. The fax phone number for official after final faxes for this Group is (703)305-3599, for all other official faxes the number is (703)305-7718, and for unofficial faxes the number is (703) 305-3602.

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0651.

  
David A. Simmons  
Supervisory Patent Examiner  
Technology Center 1700

  
B. Morrison  
September 9, 1999

<b>Notice of References Cited</b>				Application No. <b>09/106,602</b>		Applicant <b>Yang et al.</b>	
				Examiner <b>Betsy Morrison</b>		Group Art Unit <b>1724</b>	
<b>U.S. PATENT DOCUMENTS</b>							
		DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	
A		5,942,126	8/99	Dallmier et al.	210	756	
B		5,817,888	10/98	Elnagar et al.	568	656	
C							
D							
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K							
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<b>FOREIGN PATENT DOCUMENTS</b>							
		DOCUMENT NO.	DATE	COUNTRY	NAME	CLASS	SUBCLASS
N							
O							
P							
Q							
R							
S							
T							
<b>NON-PATENT DOCUMENTS</b>							
		DOCUMENT (including Author, Title, Source, and Pertinent Pages)					DATE
U							
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W							
X							



In the United States Patent and Trademark Office

Applicant: Shunong Yang, et al.

Serial No: 09/106,602

Date Filed: 9/14/99

Invention: Stable Oxidizing Bromine Formulations,  
Method of Manufacture and Uses  
Thereof for Biofouling Control

) Response to  
) Office Action of 9/14/99  
)  
) Group Art Unit: 1724  
) Examiner: B. Morrison  
)  
) Docket No: 5458  
)  
)

Honorable Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

[ X ] **AUTHORIZATION TO PAY AND PETITION FOR THE ACCEPTANCE OF ANY NECESSARY FEES:** If any charges or fees must be paid in connection with the following Communication (including but not limited to the payment of issue fees), they may be paid out of our deposit account No. 14-0105. A **duplicate copy of this sheet is enclosed.** If this payment also requires a Petition, please construe this authorization to pay as the necessary Petition which is required to accompany the payment.

**CERTIFICATE OF MAILING**

**37 C.F.R. 1.8**

I hereby certify that this correspondence is being deposited with the U.S. Postal Service as First Class Mail in an envelope addressed to: Commissioner of Patents & Trademarks Washington, D.C. 20231, on the date below:

12/13/99

Date

*Denise Ellison*

Denise Ellison

Dear Sir:

This is in response to the Office Action mailed on September 14, 1999.

REMARKS

Claims 1-57 are pending in this application. Claims 1-8, 20, 23-29 and 41 were rejected and claims 9-19, 21, 22, 30-40, 42, 43 and 47-57 were withdrawn from consideration. Claims 44-46 were allowed. Applicants affirm the provisional election to prosecute the invention of Group I, claims 1-8, 20, 23-29, 41 and 44-46 without traverse.

The Examiner has rejected claims 1-8 and 20 under 35 U.S.C. 103(a) as being unpatentable over Dallmier et al. (U.S. Patent No. 5,942,126). Applicants respectfully traverse the Examiner's rejection.

Dallmier et al. teach a method for preparing a stabilized hypobromite solution. The Dallmier et al. method calls for a specific order of addition, namely (a) mixing an aqueous solution of an alkali or alkaline earth metal hypochlorite with a bromide ion source; (b) allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form an unstabilized alkali or alkaline earth metal hypobromite solution; (c) adding a stabilizer to the unstabilized hypobromite solution; and (d) recovering a stabilized aqueous alkali or alkaline metal hypobromite solution.

In contrast, the method of Applicants' invention calls for mixing an alkali or alkaline earth metal bromide and an alkali or alkaline earth metal bromate in water to provide an aqueous solution, cooling the solution to less than 25°C, and then adding a halogen stabilizer to the solution. Dallmier et al. neither teach nor suggest the steps of Applicants' invention or their particular order. Although, as the Examiner points out, some alkali or alkaline earth metal bromide and bromate will inherently be formed during

the first step of the process of Dallmier et al., the formation of these byproducts is undesirable because they reduce the active concentration of the resulting stabilized hypobromite solution. Dallmier et al.'s process forms these byproducts because of its high pH due to the caustic nature of the hypochlorite which is added in the first step.

Unlike the teachings of Dallmier et al., Applicants do not add hypochlorite to their process. Thus, through the addition of a stabilizer at a low pH, Applicants unexpectedly discovered a way to directly convert alkali or alkaline earth metal bromide and bromate into a stable oxidizing bromine compound.

Claims 23-29 and 41 have been rejected under 35 U.S.C. §103(a) as being unpatentable over Goodenough et al. (U.S. Patent No. 3,558,503). Applicants respectfully traverse the Examiner's rejection.

Goodenough et al. disclose bromine solutions that are produced by treating an aqueous solution of bromine with a bromine stabilizer and a hydroxide, wherein the order of addition of the reagents to water or an aqueous solution of the other reagents is not critical to the operability of the invention. Goodenough et al. also teach a concentration range for the aqueous bromine solution from 0.01 to 100,000 ppm (even though theoretically a maximum of only 40,000 is possible) because the upper limit of the achievable bromine concentration by their process is defined by the maximum solubility of elemental bromine in water, i.e., about 4g/100g water or roughly 40,000 ppm. The addition of the stabilizer and hydroxide further dilute the product concentration.

In contrast, the method Applicants' invention calls for a specific order of addition, namely preparing a caustic solution comprising a halogen stabilizer, water and an alkali or alkaline earth metal hydroxide, adding bromine to the solution and cooling

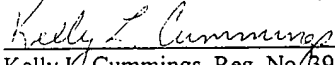


the solution. Applicants' surprisingly discovered that because of the particular order of addition, their inventive method is not limited by the elemental bromine solubility in water. Therefore, as demonstrated in Example III of the present application, a product concentration as high as 46.8% as bromine or 468,000 ppm can be achieved. Goodenough et al. neither teach nor suggest the steps of Applicants' invention or their particular order.

For the foregoing reasons, it is thought that claims 1-8, 20, 23-29 and 41 are allowable. Therefore, reconsideration and allowance are requested.

If the Examiner again rejects these claims, she is respectfully requested to call Applicants' attorney before issuing the rejection so that the patentable nature of the invention may be further discussed.


Respectfully submitted,

  
Kelly L. Cummings, Reg. No. 39,646

Nalco Chemical Company  
Patent & Licensing Department  
One Nalco Center  
Naperville, Illinois 60563-1198  
(630) 305-2328  
Date: 12/13/99

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*Amdt. 2  
entered 2/1/99*

<b>Notice of Allowability</b>	Application No. <b>09/106,602</b>	Applicant(s) <b>Yang et al.</b>	
	Examiner <b>Betsey Morrison</b>	Group Art Unit <b>1724</b>	

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance and Issue Fee Due or other appropriate communication will be mailed in due course.

☒ This communication is responsive to the response filed on Dec 16, 1999.

☒ The allowed claim(s) is/are 1-8, 20, 23-29, 41, and 44-46 (renumbered as 1-20).

☐ The drawings filed on \_\_\_\_\_ are acceptable.

☐ Acknowledgement is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d).

☐ All ☐ Some\* ☐ None of the CERTIFIED copies of the priority documents have been received.

☐ received in Application No. (Series Code/Serial Number) \_\_\_\_\_.

☐ received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

\*Certified copies not received: \_\_\_\_\_.

☐ Acknowledgement is made of a claim for domestic priority under 35 U.S.C. § 119(e).

A SHORTENED STATUTORY PERIOD FOR RESPONSE to comply with the requirements noted below is set to EXPIRE THREE MONTHS FROM THE "DATE MAILED" of this Office action. Failure to timely comply will result in ABANDONMENT of this application. Extensions of time may be obtained under the provisions of 37 CFR 1.136(a).

☐ Note the attached EXAMINER'S AMENDMENT or NOTICE OF INFORMAL APPLICATION, PTO-152, which discloses that the oath or declaration is deficient. A SUBSTITUTE OATH OR DECLARATION IS REQUIRED.

☐ Applicant MUST submit NEW FORMAL DRAWINGS

☐ because the originally filed drawings were declared by applicant to be informal.

☐ including changes required by the Notice of Draftsperson's Patent Drawing Review, PTO-948, attached hereto or to Paper No. \_\_\_\_\_.

☐ including changes required by the proposed drawing correction filed on \_\_\_\_\_, which has been approved by the examiner.

☐ including changes required by the attached Examiner's Amendment/Comment.

Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the reverse side of the drawings. The drawings should be filed as a separate paper with a transmittal letter addressed to the Official Draftsperson.

☐ Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Any response to this letter should include, in the upper right hand corner, the APPLICATION NUMBER (SERIES CODE/SERIAL NUMBER). If applicant has received a Notice of Allowance and Issue Fee Due, the ISSUE BATCH NUMBER and DATE of the NOTICE OF ALLOWANCE should also be included.

Attachment(s)

☐ Notice of References Cited, PTO-892

☐ Information Disclosure Statement(s), PTO-1449, Paper No(s). \_\_\_\_\_

☐ Notice of Draftsperson's Patent Drawing Review, PTO-948

☐ Notice of Informal Patent Application, PTO-152

☒ Interview Summary, PTO-413

☒ Examiner's Amendment/Comment

☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material

☒ Examiner's Statement of Reasons for Allowance

*Amoti . A*

Application/Control Number: 09/106,602

Page 2

Art Unit: 1724

1. An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

Authorization for this examiner's amendment was given in a telephone interview with Ms. Kelly Cummings on February 15, 2000.

2. The application has been amended as follows:

Claims 9-19, 21, 22, 30-40, 42, 43 and 47-57 have been canceled.

3. The following is an examiner's statement of reasons for allowance:

Claims 44-46 are allowed for the reasons set forth in the previous Office Action.

Claims 1-8 and 20 are allowed because the prior art of record fails to teach, disclose, or fairly suggest a method for making a stable, oxidizing bromine compound comprising mixing an alkali or alkaline earth metal bromide and alkali or alkaline earth metal bromate to provide an aqueous solution, followed by cooling, and then followed by adding a specific stabilizing compound. It is submitted that Dallmier et al., U.S. Patent No. 5,942,126, disclose a process for producing a stable hypobromite solution that comprises adding stabilizers to an aqueous solution made by adding alkali or alkaline earth metal hypochlorite with a bromide ion source. However, it would not have been obvious to one of ordinary skill in the art to have modified the process of Dallmier et al. by following the specific steps in the specific order of the instant claims, nor is any motivation provided by the disclosure of Dallmier et al. for one of ordinary skill in the art to do so.

Art Unit: 1724

Claims 23-29 and 41 are allowed because the prior art of record fails to teach, disclose, or fairly suggest a method for making a stable, oxidizing bromine compound comprising preparing a caustic solution of a specific halogen stabilizer, water, and an alkali or alkaline earth metal hydroxide, subsequently adding bromine to the solution while mixing the solution, followed by cooling the solution. It is submitted that the prior art methods for producing a stable compound containing bromine do include a step of adding a stabilizer, such as the stabilizers of instant claim 1. However, the prior art methods do not disclose a step of preparing the specific caustic solution of instant claim 1, followed by adding bromine and then cooling, nor do the prior art methods provide any motivation for one of ordinary skill in the art to do so.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

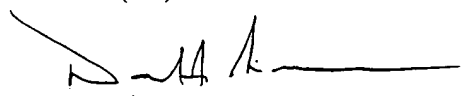
4. The prior art made of record and not relied upon is considered pertinent to Applicant's disclosure.

5. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Betsey Morrison whose telephone number is (703) 305-3934. The examiner can normally be reached on Monday through Thursday from 8:30 AM to 6:00 PM, and on alternate Fridays from 8:30 AM to 5:00 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Mr. David Simmons, can be reached at (703) 308-1972. The fax phone number for official after final faxes for this Group is (703)305-3599, for all other official faxes the number is (703)305-7718, and for unofficial faxes the number is (703) 305-3602.

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0651.

Bgm.  
B. Morrison  
February 15, 2000

  
David A. Simmons  
Supervisory Patent Examiner  
Technology Center 1700



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

## NOTICE OF ALLOWANCE AND ISSUE FEE DUE

JOHN A. CUMMINGS  
JOHN A. CUMMINGS & ASSOCIATES  
1000 CHEMICAL COMPANY  
SUITE 100  
CHICAGO, IL 60654

APPLICATION NO.	FILING DATE	TOTAL CLAIMS	EXAMINER AND GROUP ART UNIT	DATE MAILED
06/29/98	06/29/98	10	MORRISON, B	1724
First Named Applicant	Term ext. = 0 Days.			

TITLE OF INVENTION: **SOLE OXIDIZING BRONZE**  
METHOD OF MANUFACTURE AND USE  
OF BRONZE FOR BIOFOULING PROTECTION

ATTY'S DOCKET NO.	CLASS-SUBCLASS	BATCH NO.	APPLN. TYPE	SMALL ENTITY	FEE DUE	DATE DUE
252-100	252-100	100	UTILITY	NO	\$1210.00	09/15/98

**THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED.**

**THE ISSUE FEE MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED.**

### HOW TO RESPOND TO THIS NOTICE:

**I. Review the SMALL ENTITY status shown above.**

If the SMALL ENTITY is shown as YES, verify your current SMALL ENTITY status:

- A. If the status is changed, pay twice the amount of the FEE DUE shown above and notify the Patent and Trademark Office of the change in status, or
- B. If the status is the same, pay the FEE DUE shown above.

If the SMALL ENTITY is shown as NO:

- A. Pay FEE DUE shown above, or
- B. File verified statement of Small Entity Status before, or with, payment of 1/2 the FEE DUE shown above.

- II. Part B-Issue Fee Transmittal should be completed and returned to the Patent and Trademark Office (PTO) with your ISSUE FEE. Even if the ISSUE FEE has already been paid by charge to deposit account, Part B Issue Fee Transmittal should be completed and returned. If you are charging the ISSUE FEE to your deposit account, section "4b" of Part B-Issue Fee Transmittal should be completed and an extra copy of the form should be submitted.**

- III. All communications regarding this application must give application number and batch number. Please direct all communications prior to issuance to Box ISSUE FEE unless advised to the contrary.**

**IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.**

PATENT AND TRADEMARK OFFICE COPY.  
\*TOL-85 (REV. 10-96) Approved for use through 06/30/99. (0651-0033)

**PART B—ISSUE FEE TRANSMITTAL**

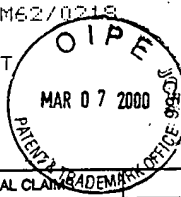
Complete and mail this form, together with applicable fees, to: **Box ISSUE FEE**  
**Assistant Commissioner for Patents**  
**Washington, D.C. 20231**

**MAILING INSTRUCTIONS:** This form should be used for transmitting the ISSUE FEE. Blocks 1 through 4 should be completed where appropriate. All further correspondence including the Issue Fee Receipt, the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Legibly mark-up with any corrections or use Block 1)

KELLY L CUMMINGS  
 PATENT & LICENSING DEPARTMENT  
 NALCO CHEMICAL COMPANY  
 ONE NALCO CENTER  
 NAPERVILLE, IL 60563-1198

IM62/0218



Note: The certificate of mailing below can only be used for domestic mailings of the Issue Fee Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing.

**Certificate of Mailing**

I hereby certify that this Issue Fee Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Box Issue Fee address above on the date indicated below.

Denise Ellison (Depositor's name)  
 Denise Ellison (Signature)  
 3/2/00 (Date)

APPLICATION NO.	FILING DATE	TOTAL CLAIMS	EXAMINER AND GROUP ART UNIT	DATE MAILED
09/106,602	06/29/98	020	MORRISON, B 1724	02/18/00
First Named Applicant	YANG, 35 USC 154(b) term ext. = 0 Days.			

**TITLE OF INVENTION:** STABLE OXIDIZING BROMINE FORMULATIONS, METHOD OF MANUFACTURE AND USES THEREOF FOR BIOFOULING CONTROL

ATTY'S DOCKET NO.	CLASS-SUBCLASS	BATCH NO.	APPLN. TYPE	SMALL ENTITY	FEE DUE	DATE DUE
1 5458	252-186.100	I48	UTILITY	NO	\$1210.00	05/18/00

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363). Use of PTO form(s) and Customer Number are recommended, but not required.

- ☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.  
☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47) attached.

2. For printing on the patent front page, list (1) the names of up to 3 registered patent attorneys or agents OR, alternatively, (2) the name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 Kelly L. Cummings  
 2 Thomas M. Breininger  
 3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)  
 PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. Inclusion of assignee data is only appropriate when an assignment has been previously submitted to the PTO or is being submitted under separate cover. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE  
 NALCO CHEMICAL COMPANY  
 (B) RESIDENCE (CITY & STATE OR COUNTRY)  
 NAPERVILLE, ILLINOIS

Please check the appropriate assignee category indicated below (will not be printed on the patent)  
☐ Individual ☒ corporation or other private group entity ☐ government

4a. The following fees are enclosed (make check payable to Commissioner of Patents and Trademarks):

- ☐ Issue Fee  
☐ Advance Order - # of Copies \_\_\_\_\_

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- ☒ Issue Fee  
☒ Advance Order - # of Copies 10

The COMMISSIONER OF PATENTS AND TRADEMARKS IS requested to apply the Issue Fee to the application identified above.

(Authorized Signature) Kelly L. Cummings (Date) 3/2/00

NOTE: The Issue Fee will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the Patent and Trademark Office.

**Burden Hour Statement:** This form is estimated to take 0.2 hours to complete. Time will vary depending on the needs of the individual case. Any comments on the amount of time required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND FEES AND THIS FORM TO: Box Issue Fee, Assistant Commissioner for Patents, Washington D.C. 20231

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TRANSMIT THIS FORM WITH FEE

<b>Interview Summary</b>	Application No. <b>09/106,602</b>	Applicant(s) <b>Yang et al.</b>
	Examiner <b>Betsey Morrison</b>	Group Art Unit <b>1724</b>

All participants (applicant, applicant's representative, PTO personnel):

(1) Ms. Betsey Morrison (3) \_\_\_\_\_

(2) Ms. Kelly Cummings (4) \_\_\_\_\_

Date of Interview Feb 15, 2000

Type: ☒ Telephonic    ☐ Personal (copy is given to ☐ applicant    ☐ applicant's representative).

Exhibit shown or demonstration conducted:    ☐ Yes    ☒ No. If yes, brief description:

\_\_\_\_\_

Agreement ☒ was reached.    ☐ was not reached.

Claim(s) discussed: 9-19, 21, 22, 30-40, 42, 43, and 47-57

Identification of prior art discussed:

none

Description of the general nature of what was agreed to if an agreement was reached, or any other comments:

It was agreed to cancel claims 9-19, 21, 22, 30-40, 42, 43, and 47-57, which are drawn to a non-elected invention, in order to place the application in condition for allowance.

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

(A fuller description, if necessary, and a copy of the amendments, if available, which the examiner agreed would render the claims allowable must be attached. Also, where no copy of the amendments which would render the claims allowable is available, a summary thereof must be attached.)

1. ☒ It is not necessary for applicant to provide a separate record of the substance of the interview.

Unless the paragraph above has been checked to indicate to the contrary, A FORMAL WRITTEN RESPONSE TO THE LAST OFFICE ACTION IS NOT WAIVED AND MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW. (See MPEP Section 713.04). If a response to the last Office action has already been filed, APPLICANT IS GIVEN ONE MONTH FROM THIS INTERVIEW DATE TO FILE A STATEMENT OF THE SUBSTANCE OF THE INTERVIEW.

2. ☐ Since the Examiner's Interview summary above (including any attachments) reflects a complete response to each of the objections, rejections and requirements that may be present in the last Office action, and since the claims are now allowable, this completed form is considered to fulfill the response requirements of the last Office action. Applicant is not relieved from providing a separate record of the interview unless box 1 above is also checked.

Examiner Note: You must sign and stamp this form unless it is an attachment to a signed Office action.



In the United States Patent and Trademark Office

Applicant: Shunong Yang, et al.

Serial No: 09/106,602

Date Filed: 6/29/98

Invention: Stable Oxidizing Bromine Formulations, Method  
of Manufacture and Uses Thereof for Biofouling  
Control

) Art Unit: 1724  
)  
) Examiner: B. Morrison  
)  
) Docket No: 5458  
)

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT  
UNDER 37 C.F.R. §§ 1.97 and 1.98

Honorable Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

Dear Sir:

**Match and Return**

In compliance with the duty of disclosure under 37 C.F.R. § 1.56, it is respectfully requested that this Supplemental Information Disclosure Statement be entered and the references listed on attached Form PTO-1449 be considered by the Examiner and made of record. Copies of the listed references are enclosed for the convenience of the Examiner.

In accordance with 37 C.F.R. § 1.97(b), this Supplemental Information Disclosure Statement is not to be construed as a representation that a search has been made or that no other possibly material information as defined in 37 C.F.R. § 1.56(a) exists.

In accordance with 37 C.F.R. § 1.97, please charge Deposit Account No. 14-0105 in the amount of \$240.00 to cover the cost of this Supplemental Information Disclosure Statement.

Respectfully submitted,

*Kelly L. Cummings*  
Kelly L. Cummings, Reg. No. 39,646  
Date: 1/27/00  
Nalco Chemical Company  
Patent & Licensing Department  
One Nalco Center  
Naperville, Illinois 60563-1198

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**CERTIFICATE OF MAILING**  
**37 C.F.R. 1.8**

I hereby certify that this correspondence is being deposited with the U.S. Postal Service as First Class Mail in an envelope addressed to: Commissioner of Patents & Trademarks Washington, D.C. 20231, on the date below:

1/27/00 *Denise Ellison*  
Date Denise Ellison

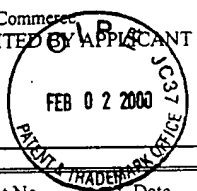
944 1724 / P

5  
9-13

09106602

02/04/2000 09:00:00 00000104 140105 240.00 CH 01 FC:133



Form PTO 1449 U.S. Dept. of Commerce LIST OF REFERENCES CITED BY APPLICANT	Atty Docket No. 54	Serial No. 09/106,602
	Applicant: Shunong Yang, et al.	
	Filing Date: 6/29/98	Group: 1724

U. S. PATENTS DOCUMENTS

Exam. Init.		Document No.	Date	Name	Class	Sub-Class	Filing date
	AA						
	AB						
	AC						
	AD						
	AE						
	AF						
	AG						
	AH						
	AI						
	AJ						
	AK						

FOREIGN PATENT DOCUMENTS

Exam. Init.		Document No.	Date	Country	Class	Sub-Class	Filing date
Bm	AL	WO 99/62339	12/99	PCT			
	AM						
	AN						
	AO						

OTHER PRIOR ART (Including Author, Title, Date, Pertinent Pages, Etc.)

	AP		
	AQ		
	AR		
	AS		
	AT		
Examiner <u>B. Hoyer</u>		Date Considered <u>9/14/00</u>	



**UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office**

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Washington, D.C. 20231

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
-----------------	-------------	----------------------	---------------------

09/106,602 06/29/90 YANG S 5459

KELLY L. CUMMINGS  
PATENT & LICENSING DEPARTMENT  
NALCO CHEMICAL COMPANY  
ONE NALCO CENTER  
NAPERVILLE IL 60563-1178

INVC/0918

EXAMINER

HOEY, B

ART UNIT

PAPER NUMBER

1724

DATE MAILED:

09/18/90

Please find below and/or attached an Office communication concerning this application or proceeding.

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PATENT APPLICATION FEE DETERMINATION RECORD Effective October 1, 1997						Application or Docket Number		
<b>CLAIMS AS FILED - PART I</b> (Column 1) (Column 2)						<b>SMALL ENTITY TYPE</b> <input type="checkbox"/> OR <b>OTHER THAN SMALL ENTITY</b>		
FOR	NUMBER FILED	NUMBER EXTRA			RATE	FEE		
BASIC FEE						395.00	OR 790.00	
TOTAL CLAIMS	57	minus 20 = 37			x\$11=		OR x\$22= 814	
INDEPENDENT CLAIMS	10	minus 3 = 7			x41=		OR x82= 574	
MULTIPLE DEPENDENT CLAIM PRESENT				+135=		OR +270=		
* If the difference in column 1 is less than zero, enter "0" in column 2				TOTAL		OR TOTAL	2178	
<b>CLAIMS AS AMENDED - PART II</b> (Column 1) (Column 2) (Column 3)						<b>SMALL ENTITY</b> OR <b>OTHER THAN SMALL ENTITY</b>		
<b>AMENDMENT A</b>	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
	Total	*	Minus	**	=		OR	
	Independent	*	Minus	***	=		OR	
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM				+135=		OR +270=	
					TOTAL ADDIT. FEE		OR TOTAL ADDIT. FEE	
<b>AMENDMENT B</b>	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
	Total	*	Minus	**	=		OR	
	Independent	*	Minus	***	=		OR	
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM				+135=		OR +270=	
					TOTAL ADDIT. FEE		OR TOTAL ADDIT. FEE	
<b>AMENDMENT C</b>	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
	Total	*	Minus	**	=		OR	
	Independent	*	Minus	***	=		OR	
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM				+135=		OR +270=	
					TOTAL ADDIT. FEE		OR TOTAL ADDIT. FEE	

\* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

\*\* If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20."

\*\*\* If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3."

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

**SIEBERTH & PATTY, L.L.C.**

*patent attorneys*

John F. Sieberth\*†  
R. Andrew Patty II\*†

Brenda C. Harvey\*

\*-Member of Michigan bar. Restricts practice to patent law.  
\*\*-Member of Louisiana and North Carolina bars.  
†-Registered before the U.S. Patent and Trademark Office.  
-Member of Louisiana bar.

2924 Brakley Drive, Suite A-1  
Baton Rouge, Louisiana 70816  
phone: 225.291.4600  
facsimile: 225.291.4606  
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**DATE: May 11, 2001**

**To: USPTO  
Examiner Alton Pryor**

**VIA FAX: 1/703-308-7924  
(Page 1 of 7)**

**From: John F. Sieberth**

**Re:**

**Our ref. no.: SU-7073-J  
Your ref. no.: 09/663,788 (SU-7073-J)**

**Message: Please see attached the proposed claims per our discussions.**

**Recipient: Please sign and date below and acknowledge by return facsimile safe receipt of this transmission. If there are any difficulties please advise.**

**Signed: \_\_\_\_\_ Date: \_\_\_\_\_**